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ON SOME ABNORMAL FREEZING-POINT LOWERINGS PRODUCED BY CHLORIDES AND BROMIDES OF THE ALKALINE EARTHS.

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Jones and Mackay,[1] in their work on solutions of double sulphates, used both the conductivity and freezing-point methods to determine the condition of these substances in solution. Jones and Ota,[2] in their work on the double chlorides, attempted to follow the same plan. They succeeded in applying the conductivity method to the solutions of double chlorides and their constituents, but were not able to get satisfactory results with the freezing-point method. The results were irregular in the case of the double salts, and did not point to any definite conclusion. Jones and Knight[3] extended the work of Jones and Ota to a number of double chlorides and bromides, and again attempted to apply the freezing-point method in the same connection. They also obtained unsatisfactory results in the cases of a number of double salts, and found, for some of the constituents, that the molecular lower-

[1] This JOURNAL, **19**, 83.
[2] *Ibid.*, **22**, 5.
[3] *Ibid.*, **22**, 110.

ing increased with increase in concentration from a certain dilution, and then increased again from this point with the dilution, as would be expected. The increase in the molecular lowering became very marked at great concentrations, indeed, so pronounced that the molecular lowering of a normal solution was as great as, or greater than, the theoretical molecular lowering when all of the salt was completely dissociated.

This was evidently a phenomenon worthy of careful study, and we undertook the investigation which will now be described. Before beginning experimental work we examined the literature to ascertain what had been done bearing upon this point.

Arrhenius,[1] in applying the freezing-point method to the then newly proposed theory of electrolytic dissociation, found the following freezing-point lowerings for a few solutions of calcium, strontium and magnesium chloride, and cadmium iodide:

$CaCl_2$.		$SrCl_2$.		$MgCl_2$.		CdI_2.	
Concentration.	Molec. low.	Concentration.	Molec. low.	Concentration.	Molec. low.	Concentration.	Molec. low.
0.0476	5.17	0.043	5.37	0.0532	5.13	0.0544	2.96
0.119	4.95	0.107	4.89	0.133	5.02	0.136	2.35
0.199	5.01	0.214	4.92	0.322	5.33	0.342	2.09
0.331	5.16	0.356	5.03	0.537	5.70	0.684	2.19

In each of these cases the molecular lowering increases with the concentration, from a certain point, and then increases from this same point with the dilution. The data are, however, too meager to warrant conclusions to be drawn from them. Further, when this work was done the freezing-point method was so imperfectly developed, that errors of considerable magnitude are necessarily present in the results.

From the work of Arrhenius, it seems probable that a minimum in the freezing-point lowering exists in a few other salts.

An increase in the molecular lowering with increase in concentration was also observed by Arrhenius[2] in the cases of four organic compounds, glycerin, mannite, dextrose, and cane-sugar. This has been subsequently[3] verified by one of us[1] for cane-sugar and dextrose.

[1] Ztschr. phys. Chem., **2**, 496.
[2] *Ibid.*, **2**, 495.
[3] Jones: *Ibid.*, **12**, 642.

A possible explanation of the increase in molecular lowering, from a certain point, with increase in concentration, has been offered by Arrhenius[1] for the non-electrolytes.

In the formula for osmotic pressure :

$$\pi = AK + BK^2.$$

π is the osmotic pressure, A is the product of the gas constant R into the absolute temperature, B is a new constant, which gives the difference between the following attractive forces : That between the solvent and dissolved substance, and that of dissolved substance for itself. K is the concentration.

If the concentration K is small, BK^2 with respect to AK is small, and we have the law for an ideal gas. But if K increases, the osmotic pressure would, relatively, increase or decrease as B is positive or negative. But with water as a solvent, B is, in general, positive. Therefore, as solutions which fulfil the above conditions increase in concentration, the osmotic pressure would increase more rapidly than the concentration, and $\frac{\pi}{K}$ would increase.

He showed later, in the same communication, that proportionality exists between osmotic pressure and freezing-point lowering. Since freezing-point lowering is proportional to osmotic pressure, $\frac{E}{K}$ would increase (E = lowering), and this agrees with experimental facts.

An increase in the molecular lowering of the freezing-point, with increase in concentration, has been observed by Loomis[2] for hydrochloric acid and magnesium chloride. He obtained the following results :

Hydrochloric acid.		Magnesium chloride.	
Concentration.	Molec. low.	Concentration.	Molec. low.
0.01	3.61	0.01	5.14
0.02	3.60	0.02	5.07
0.05	3.59	0.05	4.98
0.10	3.546	0.10	4.948
0.20	3.565	0.15	4.965
0.30	3.612	0.20	5.019
		0.25	5.079
		0.30	5.186

[1] Ztschr. phys. Chem., **10**, 51.

[2] Wied., Ann., **57**, 503.

Loomis did not obtain any evidence of a minimum of molecular lowering with barium chloride. He concluded from his extensive work on freezing-point lowerings, that "the molecular lowering continually increases with the dilution. The only exceptions are $MgCl_2$ and HCl in the region of stronger concentration. Both show a minimum value of the molecular lowering at $m = 0.10$ (m = concentration normal). This minimum is pronounced with $MgCl_2$, it is much less striking with HCl but is just as certain. To avoid any possible doubt in reference to the minimum with hydrochloric acid, the value of the molecular lowering for 0.3 normal was determined. This shows with certainty the position of the minimum at approximately 0.1 normal."

The work which has been done hitherto is thus evidently fragmentary, and shows that for a few substances there is a minimum of molecular lowering. But no generalization whatever can be made from what has thus far been done. Are these abnormal results peculiar to a substance here and there, regardless of its chemical nature, or are they confined to some group of compounds? Do substances which are chemically allied show this peculiarity, or is it due to some physical property or properties of the compounds? It is with the hope of answering such questions as these that we have taken up a systematic study of the problem.

It is well known that the alkaline halides give normal freezing-point lowerings, *i. e.*, the molecular lowering increases with the dilution from the greatest concentrations which have been studied. It is also very probable from what has already been done, that cadmium chloride gives normal lowerings of the freezing-point. Since abnormal values had already been observed by Jones and Knight for one or two members of the calcium group (the alkaline earths), we determined to study this group more thoroughly. We have therefore measured the lowering of the freezing-point of water produced by calcium chloride, barium chloride, strontium chloride, and magnesium chloride. In order to see whether the same abnormal values were obtained with cadmium, we also measured the freezing-point lowerings of fairly concentrated solutions of cadmium chloride.

In measuring the freezing-point lowerings produced by the above compounds, care was taken to keep the temperature of the freezing-bath only a little below the temperature at which the solution froze. Indeed, the bath was always kept at the highest temperature at which it was possible to freeze the solution. The difference between the temperature of the bath and that of the solution when it froze was always less than 2°.

A number of experiments were made to determine the effect of the temperature of the bath on the freezing-point of the solution. While the molecular lowering of dilute solutions changed very appreciably with change in the temperature of the bath, this was not observed with the more concentrated solutions. A change of 5° or 6° in the temperature of the bath, changed the molecular lowering of the most concentrated solutions to only a slight extent. This is what we might expect, since the magnitude of the quantity measured is so much smaller for the more dilute solutions. The apparatus used was essentially that described by Beckmann, with some slight changes.

The results which we obtained for the chlorides named above, are given in the following tables. The most concentrated solution of each chloride was standardized gravimetrically by determining one of the constituents. From this, all of the remaining dilutions were prepared. Column I gives the concentration of the solution in terms of normal, column II the observed lowering of the freezing-point, column III the correction for ice separation, column IV the correct lowering of the freezing-point, and column V the molecular lowering.

Calcium Chloride (*110.9*).

I.	II.	III.	IV.	V.
0.102	0.519°	0.011°	0.508°	4.98
0.153	0.770	0.018	0.752	4.91
0.204	1.045	0.033	1.012	4.96
0.255	1.294	0.027	1.267	4.97
0.306	1.577	0.040	1.537	5.02
0.408	2.124	0.020	2.104	5.16
0.510	2.724	0.043	2.681	5.26
0.612	3.397	0.049	3.348	5.47

Strontium Chloride (158.6).

I.	II.	III.	IV.	V.
0.05	0.265°	0.007°	0.258°	5.16
0.10	0.501	0.013	0.488	4.88
0.135	0.673	0.021	0.652	4.82
0.20	1.002	0.029	0.973	4.87
0.30	1.498	0.027	1.471	4.90
0.40	2.007	0.029	1.978	4.95
0.50	2.597	0.053	2.544	5.09
0.75	4.166	0.095	4.071	5.42

Barium Chloride (208.3).

I.	II.	III.	IV.	V.
0.0976	0.480°	0.007°	0.473°	4.85
0.1953	0.959	0.027	0.932	4.77
0.2929	1.448	0.035	1.413	4.82
0.4882	2.485	0.067	2.418	4.95
0.5858	3.005	0.060	2.945	5.03

Magnesium Chloride (95.26).

I.	II.	III.	IV.	V.
0.0508	0.287°	0.007°	0.280°	5.51
0.1016	0.550	0.013	0.537	5.28
0.1525	0.798	0.027	0.771	5.06
0.2033	1.088	0.030	1.058	5.20
0.2541	1.372	0.037	1.335	5.25
0.3801	2.055	0.040	2.015	5.30
0.5082	2.837	0.075	2.762	5.43
0.6099	3.510	0.038	3.472	5.69

Cadmium Chloride (182.9).

I.	II.	III.	IV.	V.
0.214	0.743°	0.016°	0.727°	3.39
0.322	1.051	0.029	1.022	3.18
0.429	1.342	0.044	1.298	3.03
0.643	1.862	0.030	1.832	2.85
0.858	2.369	0.040	2.329	2.72
1.072	2.908	0.023	2.947	2.65

It will be seen from the above results that the chlorides of calcium, barium, strontium, and magnesium, all have a minimum lowering which lies between 0.1 and 0.2 normal. The results for cadmium chloride show that the molecular lower-

ing increases from the most concentrated to the most dilute solution used, there being nothing to indicate the presence of a minimum in the molecular lowering.

The relations between the molecular lowerings for the above substances will be seen most readily in the following curves (Fig. I). The molecular lowerings are plotted as ordinates, the concentrations as abscissae.

The dotted portions of the curves, and the entire curve for sodium chloride introduced for the sake of comparison, are plotted from data previously obtained by one of us.[1]

Having found this minimum in the molecular lowering for the chlorides of the alkaline earths, we next turned our attention to the bromides of this group. These compounds, like the corresponding chlorides, were carefully purified, and a standard solution prepared in each case. From this solution all the remaining dilutions were made. The bromides of calcium, barium, strontium, and magnesium were studied to ascertain whether there is a minimum in the molecular lowering, and if so, at what concentration it exist. The bromide of cadmium was examined to see whether it is normal, like cadmium chloride. It is well known that the bromides of the alkalies behave normally, *i. e.*, the molecular lowering increases throughout with increase in dilution. The results which were obtained for the bromides are given in the following tables, the several columns representing the same quantities as with the corresponding chlorides :

Calcium Bromide (199.92).

I.	II.	III.	IV.	V.
0.04355	0.233°	0.005°	0.228°	5.24
0.08710	0.462	0.017	0.445	5.11
0.13065	0.686	0.022	0.664	5.07
0.17422	0.936	0.032	0.904	5.18
0.2613	1.403	0.035	1.368	5.23
0.3484	1.893	0.046	1.847	5.30
0.4355	2.421	0.024	2.397	5.50
0.5226	3.007	0.058	2.949	5.64

[1] Jones : Ztschr. phys. Chem., **11**, 113, 529.

Fig. I

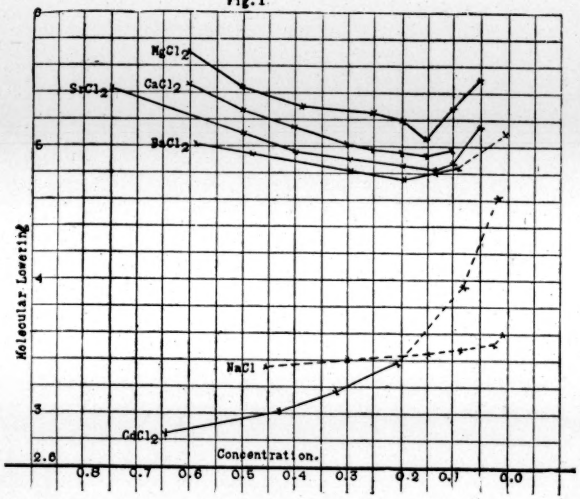
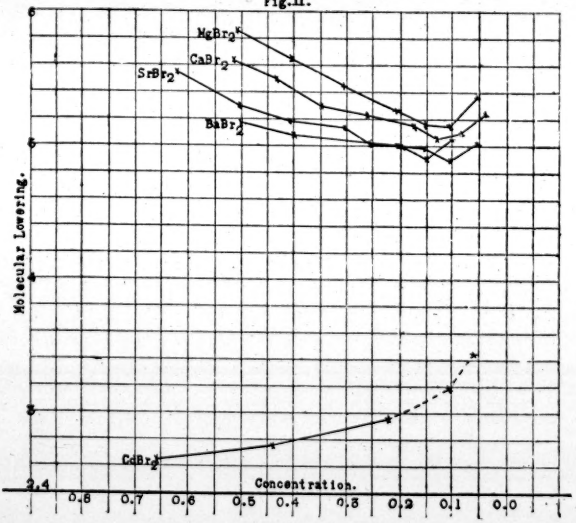

MgCl2
SrCl2
CaCl2
BaCl2
NaCl
CdCl2
Molecular Lowering.
Concentration.
2.6
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0

Fig. II.


MgBr2
CaBr2
SrBr2
BaBr2
CdBr2
Molecular Lowering.
Concentration.
2.4
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0

Strontium Bromide (*247.59*).

I.	II.	III.	IV.	V.
0.052	0.270°	0.008°	0.262°	5.04
0.103	0.521	0.018	0.503	4.88
0.155	0.795	0.022	0.773	4.98
0.207	1.062	0.027	1.035	5.00
0.259	1.327	0.019	1.308	5.05
0.310	1.615	0.023	1.592	5.13
0.414	2.203	0.056	2.147	5.19
0.517	2.781	0.040	2.741	5.30
0.621	3.516	0.069	3.447	5.55

Barium Bromide (*297.34*).

I.	II.	III.	IV.	V.
0.10	0.518°	0.012°	0.506°	5.06
0.15	0.759	0.022	0.737	4.91
0.20	1.026	0.025	1.001	5.00
0.40	2.084	0.045	2.039	5.09
0.50	2.633	0.042	2.591	5.18

Magnesium Bromide (*184.27*).

I.	II.	III.	IV.	V.
0.0517	0.283°	0.006°	0.277°	5.36
0.103	0.557	0.026	0.531	5.14
0.155	0.824	0.023	0.801	5.17
0.207	1.093	0.005	1.088	5.26
0.310	1.710	0.020	1.690	5.45
0.414	2.413	0.066	2.347	5.67
0.517	3.097	0.075	3.022	5.84

Cadmium Bromide (*272.2*).

I.	II.	III.	IV.	V.
0.22	0.665°	0.013°	0.652°	2.959
0.44	1.220	0.007	1.213	2.757
0.66	1.768	0.030	1.738	2.633
0.88	2.314	0.037	2.277	2.587

The results obtained for the bromides are plotted in curves (Fig. II), the same units being used as ordinates and abscissae as in Fig. I. The dotted portion of the curve for cadmium bromide was plotted from results previously obtained by one of us.[1]

The curves for the bromides as for the chlorides show a

[1] Jones: Ztschr. phys. Chem., **11**, 529.

distinct minimum, and all of them at about the same dilution, from 0.1 to 0.15 normal. This is almost exactly the same concentration as that at which the corresponding chlorides showed a minimum of molecular lowering. The curves of the chlorides were extended, in a number of cases, beyond the dilution used in this work, on the basis of work previously done, to show that the minimum of molecular lowering had unquestionably been reached. The results for sodium chloride were plotted on the same scale, for the sake of comparison.

The general conclusion which can be drawn from the freezing-point lowerings is that all the chlorides and bromides of the alkaline earths have a minimum of molecular lowering of the freezing-point, this minimum lying between 0.1 and 0.2 normal. Further, in very concentrated solutions these substances give a lowering of the freezing-point as great as, or greater than, the theoretical lowering, if the compounds were completely broken down into ions. These apparently abnormal results are shown neither by the alkaline halides nor by the halogen compounds of the magnesium-zinc group.

It is a little difficult to see at first sight how these results can be brought into accord with the theory of electrolytic dissociation, or interpreted in terms of it. Before attempting any explanation of these results, we determined to measure the conductivity of the same solutions whose freezing-point lowerings we had studied. The conductivities of a number of these solutions had already been measured by Jones and Knight,[1] in connection with their work on the condition of double chlorides and bromides in solution. We measured the conductivities of the more concentrated solutions of calcium and barium chlorides, and calcium, strontium, and magnesium bromides. For the conductivities of the more dilute solutions of these substances we are indebted to Mr. Caldwell, who kindly made the measurements which we desired. The conductivities of the remaining compounds had, as already stated, been measured by Jones and Knight.

We give below the molecular conductivities of the compounds which showed abnormal freezing-point lowerings, and state in each case by whom the measurements were made :

[1] This JOURNAL, **22**, 110.

Calcium Chloride.

(Chambers.)

v.	$\mu_{v\ 25°}$.
1.961	134.3
3.912	152.06
4.902	156.62
6.536	164.75
9.804	174.05
12.256	179.35
19.610	185.75
33.333	197.50
(Caldwell.)	
32.66	198.15
65.33	210.8
130.66	222.55
261.33	234.97
522.66	244.94
1045.33	246.59
2090.66	253.44
4181.33	265.73

Strontium Chloride.

(Knight.)

v.	$\mu_{v\ 25°}$.
1	108.5
2	130.0
4	146.6
8	162.6
16	179.5
40	196.1
80	207.4
160	219.0
320	229.3
640	237.6
1600	246.4
3200	252.5
6400	260.0
12800	270.0

Barium Chloride.

(Chambers.)

v.	$\mu_{v\ 25°}$.
2.013	131.45
4.026	148.37
5.033	158.44
6.711	161.14
10.063	170.62
12.580	184.85
20.130	191.16
33.558	200.88
(Caldwell.)	
33.547	203.06
67.094	213.78
134.188	224.77
268.37	237.0
536.75	248.2
1073.5	260.8
2147.0	270.3
4294.0	276.3

Magnesium Chloride.

(Knight.)

v.	$\mu_{v\ 25°}$.
1.76	126.3
3.52	143.3
7.04	159.8
14.08	175.1
35.2	190.3
70.4	201.1
140.8	211.3
281.6	221.1
563.2	227.4
1408.0	234.5
2816.0	243.2
5632.0	253.3

Calcium Bromide.

(Chambers.)

v.	$\mu_{v\ 25°}$.
2.193	151.2
4.596	170.88
5.74	174.37
11.48	189.8
14.34	191.9
22.96	201.3
38.27	210.1
(Caldwell.)	
38.27	208.2
76.54	219.8
153.08	230.3
306.2	241.2
612.3	248.8
1224.7	256.0
2449.0	262.5
4898.0	270.2

Strontium Bromide.

(Chambers.)

v.	$\mu_{v\ 25°}$.
1.932	141.33
3.864	159.46
4.831	165.7
6.439	171.6
9.661	181.5
12.08	183.9
19.32	194.1
32.20	207.7
(Caldwell.)	
32.19	208.6
64.38	221.6
128.8	231.6
257.5	244.6
515.0	254.2
1030.1	261.8
2060.2	272.5
4120.3	282.4

Barium Bromide.

(Knight.)

v.	$\mu_{v\ 25°}$.
2	147.7
4	162.4
8	176.5
16	190.9
32	202.0
80	218.5
160	228.8
320	241.5
640	249.2
1280	257.1
3200	270.8
6400	280.8

Magnesium Bromide.

(Chambers.)

v.	$\mu_{v\ 25°}$.
3.868	141.9
4.812	159.3
6.447	163.8
9.671	173.5
12.09	176.2
19.34	187.5
32.26	190.3
(Caldwell.)	
32.24	191.7
64.48	206.1
128.9	216.7
257.9	226.8
515.8	234.8
1031.6	245.0
2063.2	253.9
4126.3	257.8

For the sake of comparison, the conductivities of cadmium chloride and cadmium bromide, as measured by Knight, are also given.

Cadmium Chloride.

(Knight.)

v.	$\mu_{v\ 25°}$.
0.932	28.0
1.864	44.9
3.728	62.8
7.456	82.5
14.91	101.5
37.37	129.6
74.75	150.3
149.5	171.7
299.0	192.3
598.0	206.5
1495.0	227.6
2990.0	242.0
5980.0	255.3
11960.0	269.5

Cadmium Bromide.

(Knight.)

v.	$\mu_{v\ 25°}$.
2.60	41.3
5.20	57.4
10.40	75.7
20.80	95.1
41.60	115.3
104.0	144.2
208.0	166.0
416.0	188.8
832.0	209.3
1664.0	228.2
3328.0	242.4
6656.0	256.1

The conductivity measurements given in the above tables are plotted in curves (Figs. III and IV), that they may be compared directly with the freezing-point lowerings. The conductivities of the dilute solutions are not included in the curves, since these are far less interesting from our present point of view. The conductivity results, from the most concentrated solutions used to about 0.025 normal, are included in the curves. The part of the conductivity curve which is of special interest is that for the concentration at which the freezing-point curve shows a minimum. We wish especially to see whether there is any irregularity in the conductivity curve in this region. The molecular conductivities are plotted as ordinates, the concentrations as abscissae. The concentrations are expressed in "volumes," or the number of liters which contain a gram-molecular weight of the substance. An examination of the conductivity curves shows no irregularity in the region where the molecular lowering of freezing-point becomes a minimum. The conductivity curves are just such as would be expected for any strongly dissociated electrolyte in water. The conductivity increases regularly from the most concentrated to the most dilute solution investigated, and shows a continually increasing dissociation with increase in dilution.

Fig. III.

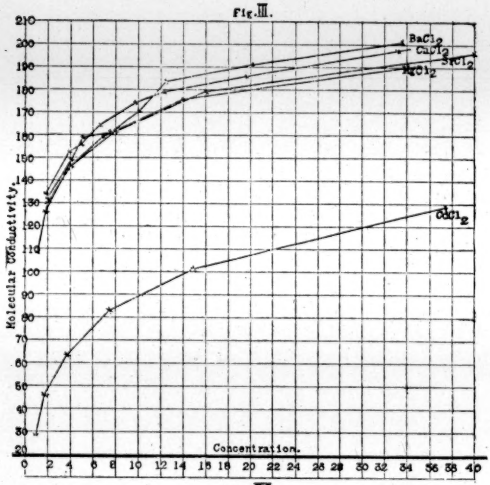
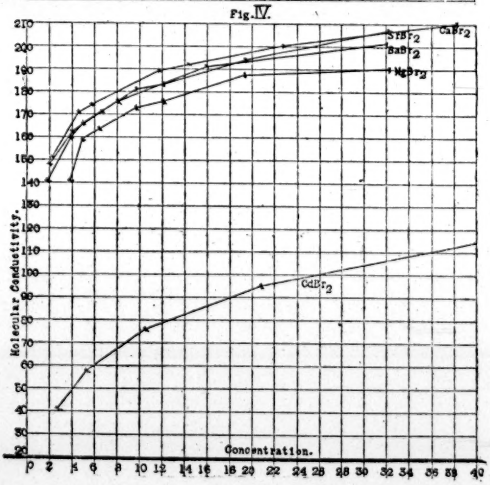


Fig. IV.



A Possible Explanation of the Abnormal Results.

The facts which have to be taken into account are these: The molecular lowering of the freezing-point increases from about 0.1 normal with increase in concentration and also with increase in dilution, there being a minimum of molecular lowering for the chlorides and bromides of the alkaline earths at about this concentration. The increase in molecular lowering with increase in dilution is normal, but the increase in the molecular lowering with increase in concentration is abnormal, and apparently at variance with the theory of electrolytic dissociation.

The conductivities of solutions of these chlorides and bromides increase, as would be expected, from the most concentrated to the most dilute solution employed.

These facts mean that the freezing-point lowering produced by concentrated solutions of these chlorides and bromides are much greater than we should expect from a consideration of the theory, especially when we take into account the fact that the dissociation of the most concentrated solutions is hardly more than 50–60 per cent, as is shown by the conductivity measurements.

How is it then possible to account for these abnormally great depressions of the freezing-point? There appears to us to be only one way. In concentrated solutions these chlorides and bromides must take up a part of the water forming complex compounds with it, and thus removing it from the field of action as far as freezing-point lowering is concerned. The compound, which is probably very unstable, formed by the union of a molecule of the chloride or bromide with a large number of molecules of water, acts as a unit, or as one molecule in lowering the freezing-point of the remaining water. But the total amount of water present, which is now acting as solvent, is diminished by the amount taken up by the chloride or bromide molecules. The lowering of the freezing-point is thus abnormally great, because a part of the water is no longer present as solvent, but is in combination with the chloride or bromide molecules. By assuming that a molecule of the halide is in combination with a large num-

ber of molecules of water, it is possible to explain all of the freezing-point results obtained.

But the conductivity results must also be taken into account. These show, unmistakably, a marked degree of dissociation even in the most concentrated solutions employed. There must, therefore, be a certain number of the molecules broken down into ions, either by the water acting as solvent, or by the water in combination with the molecules, just as salts are probably dissociated in their water of crystallization.

We know of cases where there is direct experimental proof that molecules combine with water in the more concentrated solutions, and are then dissociated with increase in dilution.

The case of sulphuric acid is especially interesting in this connection. It was shown by one of us,[1] while working in the laboratory of Arrhenius, that sulphuric acid first forms the definite hydrates, $H_2SO_4.H_2O$ and $H_2SO_4.2H_2O$, and then, on further addition of large volumes of water, it is known from the conductivity measurements that sulphuric acid breaks down completely into ions.

The existence of the hydrates was shown by the freezing-point method. Acetic acid was used as the solvent, and the lowering of its freezing-point produced by sulphuric acid alone was determined. Then the lowering of the freezing-point of acetic acid by water alone was determined, and, finally, the lowering produced by sulphuric acid and water when brought together into the acetic acid. This was never equal to the sum of the separate lowerings, and from the amount of the difference the amount of water in combination with the sulphuric acid was calculated.

It should be observed in connection with the explanation we have offered of these abnormal results, that the chlorides and bromides of the alkaline earths are, generally, very hygroscopic substances, resembling sulphuric acid in their power of attracting water. Some of them are, it is true, far more hygroscopic than others, yet, when dehydrated, they all combine readily with water. It may be due to this property that they combine with water to such an extent in concentrated solutions. It is true that the chlorides of zinc and cad-

[1] Jones: Ztschr. phys. Chem., 13, 419; This JOURNAL, 16, 1.

mium are also hygroscopic, but the halides of zinc, and especially of cadmium and mercury, behave, in general, abnormally with respect to their dissociation in water.

It should also be noted that the compound, in addition to magnesium chloride, with which Loomis found a minimum of molecular lowering—hydrochloric acid—is also very hygroscopic, attracting water with great energy.

We do not put forward the above suggestion to account for our results as a final statement of a theory, but only as tentative, and subject to modification as new facts are brought to light. It does, however, seem to account qualitatively for the experimental facts which have been brought to light.

We propose to extend this investigation to a much larger number of hygroscopic substances, to ascertain whether there is any relation between this property and abnormal freezing-point lowerings such as those recorded in this paper.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
MAY, 1899.

Contributions from the Chemical Laboratories of the Massachusetts Institute of Technology.

XXIII.—THE PREPARATION OF PURE TELLURIUM.

BY JAMES F. NORRIS, HENRY FAY, AND D. W. EDGERLY.

In testing a volumetric method[1] for the estimation of tellurium which we proposed some time ago, we were led to study the methods which had been used for the purification of tellurium. As it appeared that a substance of undoubted purity could be obtained only by a very long series of operations, which involved fusion with potassium cyanide, precipitation, and subsequent distillation in hydrogen, a new method was sought. It seemed probable that the basic nitrate of tellurium might be used for this purpose, as it is a well-crystallized compound, very easily obtained. We accordingly prepared it, and having found that the sample did not agree in some of its properties with those which had been assigned to it in the literature, a careful study of it was made. Klein and Morel[2]

[1] This JOURNAL, **20**, 278.
[2] Bull. Soc. Chim. [2], **43**, 198.

prepared the compound by dissolving tellurium in nitric acid (1.25 sp. gr.) and evaporating the solution. To the crystals which formed they assigned the formula $4TeO_2.N_2O_5.1\frac{1}{2}H_2O$. Only very small crystals were formed and these were hygroscopic. The nitrate prepared by us by the method of Klein and Morel was obtained in crystals sometimes a centimeter in length and were not hygroscopic. An analysis was accordingly made, which showed that the compound has the formula $4TeO_2.N_2O_5.H_2O$, or better $Te_2O_5(OH)NO_2$, since the water is not present as water of crystallization.

In the preparation of the nitrate it is crystallized from nitric acid, and as the impurities present in the tellurium do not form crystalline compounds under these conditions, it was thought that the salt could be obtained quite pure. The tellurium obtained from it would, as a result, be free from those substances with which it is invariably mixed when precipitated from solution by sulphur dioxide or other reducing agents. A sample of basic nitrate was recrystallized three times and then subjected to a careful study, with the result that no impurity was discovered.

On account of the fact that the most trustworthy atomic weight determinations of tellurium have given results which place it in the eighth group in the periodic system of the elements, notwithstanding its striking similarity to sulphur and selenium, the hypothesis has been put forward that tellurium is a mixture of true tellurium with an atomic weight of about 125, and another element with a higher atomic weight. Brauner,[1] who spent a number of years studying tellurium, has expressed this as his opinion.

As no known substance was found in the tellurium obtained from the pure nitrate, the element was subjected to a fractionation to determine whether it could be broken down into two or more substances by this means, which proved so effective in the case of didymium. The double bromide of tellurium and potassium, made from tellurium dioxide, hydrobromic acid, and potassium bromide prepared with the greatest care, was carried through a fractionation which involved over 200 crystallizations. In order to determine whether this fraction-

[1] J. Chem. Soc., **55**, 382; and **67**, 549.

ation had accomplished any decomposition, the tellurium from the end fractions was converted into the nitrate, and the loss in weight of the latter compound on ignition determined. Any change in atomic weight could be determined in this way. The results obtained with the two fractions were identical within the limits of accuracy of the method. The differences obtained, 0.4 of a unit in the atomic weight, was probably due to inaccuracies in the method. The conversion of the nitrate into the oxide, as at present carried out, does not appear to give results from which the atomic weight of tellurium can be determined with great accuracy.

Preparation of Basic Tellurium Nitrate.

The tellurium used was obtained from a residue obtained in the electrolytic refining of copper. This residue was a solution which consisted principally of the sodium salts of tellurous, selenous, and silicic acids, with the last-named acid in great excess. Whitehead[1] has described the process by which the copper is refined and how the liquid is obtained. Tellurium was obtained from this liquid in two ways. At first the solution was diluted with water and neutralized with sulphuric acid, which threw out a heavy white precipitate of tellurous acid and silica. This mixture was evaporated to dryness twice with hydrochloric acid to render the silica insoluble, and the residue extracted several times with strong hydrochloric acid. From the solution of the chloride so formed, the tellurium was obtained by precipitation with acid sodium sulphite. In later experiments the tellurium was precipitated from the hot alkaline solution with commercial glucose. The tellurium obtained by both methods contained silica and other impurities. The crude metal was added to warm dilute nitric acid (sp. gr. 1.25), and the resulting solution evaporated to dryness in order to insure complete removal of silica. The mixture of basic nitrate and oxide was ignited till free from nitric acid, and was then extracted a number of times with strong hydrochloric acid. The solution in hydrochloric acid was filtered through asbestos and precipitated with acid sodium sulphite. The sulphite was added slowly until the precipitate

[1] J. Am. Chem. Soc., 17, 849.

formed was black, thus showing that most of the selenium was precipitated. After the mixed precipitates of selenium and tellurium had settled, the solution was decanted, filtered, and the precipitation continued. The tellurium which had been freed from a large share of its impurities by this second precipitation was again dissolved in nitric acid (sp. gr. 1.25), and the basic nitrate obtained from the solution by crystallization. The nitrate was twice recrystallized. This was best done as follows: The salt was stirred with a large amount of nitric acid (sp. gr. 1.25) heated to about 70° C. At a higher temperature the nitrate was decomposed into a mixture of amorphous and crystalline oxide, which was not readily dissolved by the acid. The solution was filtered through asbestos and evaporated at a temperature of about 80°. In some cases the solution was allowed to cool after crystals appeared. In other cases the evaporation was continued while the crystals were separating from the liquid. By the latter method larger crystals were obtained, which were at times 0.5 cm. in length. The nitrate crystallizes in orthorhombic prisms, terminated by macrodomes and truncated by well-developed macropinacoids and small brachypinacoids. The salt is not hygroscopic, some crystals having stood in the open air for over a month without losing their bright luster.

Purity of the Basic Nitrate of Tellurium.

The purity of the basic nitrate of tellurium, which had been twice recrystallized, was studied. It was again recrystallized from nitric acid and a qualitative analysis of the crystals was made. The mother-liquor was evaporated to dryness and also analyzed. The presence of no foreign element was detected in either case. Whitehead[1] and Keller[2] have determined what substances are present in the crude copper from which the tellurium used in this work was obtained. These are silver, gold, bismuth, arsenic, antimony, and selenium. As none of these elements forms a crystalline compound which is difficultly soluble in nitric acid, it is seen that the basic nitrate of tellurium was readily obtained in pure condition. Brauner has shown that pure tellurium cannot be obtained

[1] J. Am. Chem. Soc., **17**, 849.
[2] *Ibid.*, **19**, 778.

by precipitation, and that repeated distillation of the metal is necessary to free it from the heavy metals.

In order to test for minute traces of selenium, a common impurity in tellurium, the following method was devised, based on the difference in behavior of the oxides of selenium and tellurium with hydriodic acid. The former oxide is reduced and iodine set free, while the latter is converted into the tetraiodide. The test is made in this way: About 0.15 to 0.2 gram of the oxide to be tested is dissolved in 2 cc. of a 10 per cent solution of sodium hydroxide, and 3 cc. of hydrochloric acid (sp. gr. 1.12) is added. The solution is then cooled to the room temperature, carbon bisulphide and 2 drops of a dilute solution of potassium iodide (2 grams in 100 cc. water) are added, and the tube is shaken. Under the above conditions, if selenium is present, the carbon bisulphide will be colored by the iodine liberated, and the small amount of tellurium tetraiodide formed will remain in solution. It is necessary to avoid a large amount of potassium iodide in order to prevent the formation of much tellurium tetraiodide, which would dissolve in the carbon bisulphide and so obscure the color of the iodine. Any doubt whether the color is due to liberated iodine or to tellurium tetraiodide can be decided definitely by shaking the carbon bisulphide with water. The color produced by the iodine is not altered while the tellurium tetraiodide is decomposed and the carbon bisulphide again becomes colorless. The accuracy of the method was tested by mixing known amounts of selenium dioxide with the tellurium to be tested. Using the amounts given above, 0.0012 mg. selenium can be detected in the presence of 0.160 gram of tellurium dioxide, that is about 1 part in 150,000. No selenium could be detected in the oxide obtained from the pure nitrate when this very delicate test was applied.

It is of interest to note here that a strong solution of potassium iodide acidified with hydrochloric acid, is a very delicate test for tellurium. The dark color produced is quite characteristic, resembling somewhat in strong solution the color of platinum solutions containing iodides. The difference is readily shown, however, by dilution, when the color produced by platinum persists as a pink, while the color pro-

duced by the tellurium disappears on account of the decomposition of the iodide.

No foreign substance was found in the tellurium from the nitrate by careful qualitative analysis, yet it was subjected to additional tests. Brauner and Wills found that the purest tellurium obtained by precipitation invariably left a residue when distilled in hydrogen. A sample of the oxide prepared from the nitrate was dissolved in pure hydrochloric acid and the tellurium precipitated with sulphur dioxide and washed until free from hydrochloric acid. The tellurium was then distilled in a stream of hydrogen, which was prepared by the action of sulphuric acid on zinc. The gas was purified by the method used by Wills[1] in preparing pure tellurium for a determination of its atomic weight. After the distillation a bright stain was left on the porcelain boat. The tellurium was redistilled a number of times with the same result. The gray, shiny spot on the boat was not affected by hot sodium hydroxide, hydrochloric, or nitric acid, and was not volatilized by the heat of a blast-lamp.

From the following experiments it was shown that this residue was due to the union of a small amount of tellurium with the porcelain of the boat at the high temperature required for the distillation. Some tellurium prepared from the nitrate was next distilled in a vacuum. After the first distillation a light gray substance was left in the boat. This was flocculent, dissolved completely in dilute hydrochloric acid and sodium hydroxide, and evidently was tellurium dioxide, which is always present in precipitated tellurium. The tellurium, when redistilled in vacuum, left no residue, but when distilled in hydrogen a stain was left on the boat as before. Some pure tellurium, obtained by distillation in a vacuum, was heated on porcelain in a blast-lamp flame. A stain was left which was caused by the combination of a small amount of the tellurium with the porcelain. This does not take place when the metal is distilled in a vacuum as the temperature of distillation is lower.

The oxide prepared from the nitrate was also completely volatile without leaving a residue. It was heated to redness

[1] J. Chem. Soc., **35**, 704.

on a platinum foil placed inside of a porcelain crucible. The above experiments show that a careful examination of the tellurium obtained by recrystallization of the basic nitrate did not show the presence of any known substance.

Analysis of Basic Tellurium Nitrate.

As the basic nitrate obtained by crystallization from nitric acid is a stable substance, and is not hygroscopic as Klein and Morel have reported, a careful analysis of it was considered necessary. The water was determined by igniting the substance, which had been previously dried at 120°, in a current of oxygen for two hours. In the front part of the tube was placed metallic copper to reduce the oxides of nitrogen. The nitrogen was estimated by a method which was essentially that of Dumas. The tellurium dioxide was determined by heating the nitrate slowly until all of the oxides of nitrogen were given off, and then fusing quickly the oxide left. The decomposition of the nitrate was accomplished most conveniently by placing the platinum crucible inside of a larger porcelain crucible, which was heated by a Bunsen burner. After an hour's heating the oxide was in the form of a loose white powder. The results of the analyses follow:

I. 0.7975 gram substance gave 23.25 cc. N at 0° and 760 mm. pressure.

II. 1.2222 gram substance gave 37.20 cc. N at 0° and 760 mm. pressure.

I. 2.0530 gram substance gave 0.0538 gram H_2O.

II. 2.2981 gram substance gave 0.0590 gram H_2O.

I. 0.9491 gram substance gave 0.7925 gram TeO_2.

II. 0.9920 gram substance gave 0.8282 gram TeO_2.

	Calculated for $4TeO_2.N_2O_5.1\frac{1}{2}H_2O$.	Calculated for $4TeO_2.N_2O_5.H_2O$.	Found. I.	Found. II.
N	3.62	3.66	3.64	3.84
H_2O	3.49	2.36	2.62	2.57
TeO_2	82.54	83.52	83.49	83.36

The atomic weight of tellurium has been taken as 127.6 in calculating the above results. Klein and Morel,[1] using 129 as the atomic weight of tellurium, obtained these results:

[1] Bull. Soc. Chim. [2], **43**, 198.

	Calculated for $4TeO_2.N_2O_5.1\frac{1}{2}H_2O$.	Found. I.	Found. II.
N	3.59	3.70	....
H_2O	3.47	2.90	3.80
TeO_2	82.66	82.20	83.30
Te	65.57	66.10	66.50

Experiments described below show that there is no water of crystallization in the compound. The formula therefore is best written $Te_2O_3(OH)NO_3$.

Decomposition of Basic Tellurium Nitrate by Heat.

Two samples of the nitrate were heated at gradually increasing temperatures in order to determine whether the hydrogen in the compound is present as water of crystallization. The substance was heated for two or more hours at intervals of 10°, beginning at 110°. If at the end of that time the weight had changed, the heating was continued without changing the temperature until constant weight was obtained. The results follow:

Number of hours heated.	Temperature.	Percentage loss. I.	Percentage loss. II.
12	110°–170°	0.00	0.00
2	170°–180°	0.07	0.03
4	180°–190°	0.42	0.26
11	190°–200°	2.47	3.36
9	200°–210°	3.71	4.15
9	210°–220°	4.02	5.85
6	220°–230°	8.00	9.67
9	230°–250°	8.60	10.30
1	About 350°	16.51	16.50

From the above results it will be seen that there is no loss of weight up to 170°, when a slight decomposition begins. At 190° oxides of nitrogen begin to be evolved. There was no distinct point at which the water was given off. The decomposition was gradual, both water and nitric acid being given off at the same time. The figures in the last line of the table give the results of heating two portions of the nitrate in covered platinum crucibles protected by porcelain crucibles. The results are practically the same as those obtained in the very accurate determinations described later; *viz.*, 16.47. The oxide which was left was tested for nitric acid by phenol-sul-

phonic acid, and only a trace was found. It is therefore unnecessary to fuse the oxide in making a gravimetric estimation of tellurium, if it is heated in the manner described. The loss which accompanies fusion can be done away with and more accurate results obtained. The experiments recorded above are not in accord with the statement of Klein and Morel that the nitrate begins to decompose at the fusing-point of lead.

Action of Nitric Acid on the Nitrate.

In recrystallizing the nitrate it was observed that at times a residue was left which dissolved with difficulty in nitric acid. This residue examined under the microscope showed well-developed crystals in the form of octahedra, and, when ignited, it did not lose in weight. The nitrate was changed into a mixture of amorphous and crystalline tellurium dioxide. It was therefore important to study the conditions of formation of the oxide in order to be able to get crystals of the nitrate in perfectly pure condition.

Some nitrate was heated with not enough nitric acid (sp. gr. 1.20) to dissolve it. After the acid had boiled twenty-five minutes the residue was examined and found to contain no nitrate. From the hot solution a small amount of white amorphous powder separated. On evaporation of the nitric acid solution well-defined crystals of the nitrate were formed. These were shown by analysis to be free of oxide. The loss in weight on ignition was 16.51 per cent. Theory requires a loss of 16.48 per cent. The same results were obtained when nitric acid of specific gravity 1.25 was used. It will be seen, therefore, that, while the dilute acids decompose the nitrate, any crystals which are formed from it by concentration are pure nitrate. The reasons for the directions given above for the recrystallization of the nitrate, are now evident. The nitrate is stirred with the acid (sp. gr. 1.25) at about 70° in order to avoid decomposition into the oxide, and saturation of the solvent. Crystals of the nitrate increase markedly in size when heated with concentrated boiling nitric acid, and a large amount crystallizes from the oxide on cooling.

Electrolytic Deposition of Tellurium.

Schucht[1] and Whitehead[2] have shown that tellurium is deposited by the electric current from an acid or alkaline solution. Numerous attempts were made to get the conditions under which the deposit would be made in such a form that it could be weighed. It was deposited from hydrochloric and nitric acid solutions and from solutions of the alkali tellurites. As tellurium is nearest to antimony in the electrolytic scale, the conditions under which antimony is deposited were applied to tellurium. The precipitate was always in an amorphous, flocculent condition. Some tellurium which had been deposited by electrolysis was converted into the nitrate and the loss in weight on ignition determined. This was done to determine whether the electrolysis had effected any decomposition of the element. As the loss in weight was 16.55 per cent, it was concluded that no decomposition had taken place.

Fractional Crystallization of Potassium Bromtellurate.

Owing to the uncertainty of the homogeneity of tellurium it was subjected to a careful fractionation. Wills[3] fused tellurium with potassium cyanide and precipitated the element in two fractions from the aqueous solution of the telluride by a current of air. Brauner used this same process but separated the tellurium into four fractions. He also precipitated tellurous acid in eight portions from a solution of tellurium tetrachloride, and subjected tellurium tetrabromide to fractional sublimation in a vacuum. The details of the latter method are not given.

Staudenmaier[4] crystallized telluric acid and collected the compound in four portions. In all cases atomic weight-determinations of the fractions gave no evidence of a breaking down of the tellurium.

The importance of testing the hypothesis of the compound nature of tellurium led us to undertake a more careful fractionation than had been accomplished heretofore. The results of Wills, Brauner, and Staudenmaier are not conclusive, since the fractionation was not carried far enough in any case

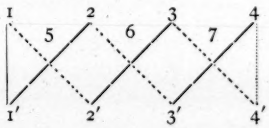
[1] Jahresbericht, 1883, 222, 1514.
[2] J. Am. Chem. Soc., **17**, 849.
[3] J. Chem. Soc., **35**, 704.
[4] Ztschr. anorg. Chem., **10**, 189.

to warrant definite conclusions. Crystallization was selected as the means of fractionation, as it appears to be much more efficient than precipitation. A number of compounds were studied with the view of using them for this purpose. The organic compounds formed by tellurium tetrachloride with anisol and phenetol, $TeCl_2(C_6H_4.OCH_3)_2$, $TeCl_4(C_6H_4OC_2H_5)_2$, were prepared. They are described as crystallizing well. The progress of the crystallization could be easily watched as the compounds have distinct melting-points. It was found extremely difficult, however, to prepare these compounds in large quantities and to recrystallize them.

The salt finally selected was the double bromide of tellurium and potassium. This salt is readily prepared and crystallizes well from water. In order to have the results of the fractionation as conclusive as possible all the reagents used were prepared with the greatest care.

Potassium bromide was prepared by heating chemically pure potassium bromate of commerce which had been recrystallized four times. Hydrobromic acid was made by Squibb's method, and purified by four redistillations from potassium bromide. The tellurium dioxide was made from basic nitrate which had been recrystallized three times from nitric acid. The nitrate was decomposed at about 350° and then fused in portions of 6 to 10 grams in a platinum crucible protected by a larger porcelain crucible. Theoretical quantities of tellurium dioxide and potassium bromide were dissolved in hydrobromic acid and the salt obtained by crystallization. Throughout the work porcelain dishes alone were used. Eight hundred grams of this compound were then subjected to fractional crystallization.

The following diagram may help to make the scheme of fractionation clear. Crystals are represented by solid lines and mother-liquors by dotted lines:



Four portions of 200 grams each were dissolved in water, usually containing a small amount of hydrobromic acid, and the solutions evaporated to such a point that about 100 grams of salt separated on cooling. The salt from fraction 1 was set aside; the salt from fraction 2 was added to the mother-liquor of fraction 1, making number 5; the salt from number 3 was added to the mother-liquor from number 2; and the salt from 4 was added to mother-liquor number 3. The mother-liquor from fraction 4 was set aside during the intermediate crystallization of fractions 5, 6, and 7. These solutions were evaporated as before. The salt from fractions 1 and 5 were united, making the first portion of the second series. The mother-liquor of number 5 and the crystals from 6 made number 2 of the second series. The mother-liquor of 6 and the crystals from 7 made number 3, and finally the mother-liquors of 4 and 7 made number 4 of the second series. It will be seen that a complete series involves seven crystallizations. This procedure of adding the crystals of one fraction to the mother-liquor of another tends to make the most soluble and the least soluble portions collect in the end fractions. The fractionation was repeated thirty times, which involved 215 crystallizations.

There were no indications during the work of any change in the salts, so an atomic weight determination of the tellurium from the end fractions had to be made. More than fifteen different methods have been studied in attempting to determine the atomic weight of tellurium, and of these but one method, the determination of bromine in the tetrabromide, was found to give concordant results. As the use of this method is not free from objections, and involves a large amount of work, a simpler method was sought. Very concordant results were obtained in the analysis of the basic nitrate when it was changed to the oxide by ignition, and it seemed possible that trustworthy results, which would show any variations in the atomic weight, might be obtained, if the ratio between the nitrate and oxide was determined with great care.

As Klein and Morel have stated that the nitrate is hygroscopic, experiments were made with a pure sample to test this

point. Two portions of the salt were heated for eight hours at 120° in platinum crucibles, transferred to a desiccator, and after cooling were weighed immediately, a platinum crucible being used as a tare. After standing half an hour and fifteen hours in the balance case, the crucibles were weighed again, with the following results:

Hours.	A.	B.
0	1.96242	2.19839
0.5	1.96275	2.19860
15.0	1.96274	2.19855

It will be seen that the weights remained perfectly constant after the crucibles had stood long enough to be in equilibrium with the atmosphere of the balance case, which shows conclusively that the salt is not hygroscopic. It was then heated at 120° for varying periods of time to determine whether it could be brought to constant weight.

Hours heated.	A.	B.
2.5	2.28692	2.12905
14.0	2.28667	2.12897
7.5	2.28676	2.12896
7.0	2.28672	2.12905

The above results show that this could be done very satisfactorily.

The preliminary experiments on the decomposition of the nitrate showed that the oxides of nitrogen evolved during heating carried off a small amount of tellurium dioxide mechanically. In order to avoid this loss the following device was used: A platinum crucible was provided with two removble platinum disks which fitted the crucible at distances of about one-half and one inch from the bottom. In the center of the lower disk a hole was cut about one-eighth inch in diameter. The salt was placed in the crucible, the disks adjusted, and the cover put on. There were three surfaces over which the issuing gases had to pass, and on these the oxide carried along was deposited. In the experiments a slight dullness was visible on the upper disk, but the cover was bright, thus showing that no oxide had reached it.

The nitrate was decomposed slowly in order to avoid a rush of gas. It was heated for two hours at 200°, 250°, and 300°;

three hours at 350°, 400°, 450°, 500°, and 550°; and was finally fused quickly in the oxidizing flame of a Bunsen burner.

The tellurium from the two end fractions of the fractional crystallization was converted into nitrate. The salt was moistened with concentrated nitric acid when being ground in order to prevent decomposition from atmospheric moisture. The finely divided nitrate was heated to constant weight and converted into the oxide in the manner described above.

The results of the analysis of the nitrate prepared from the tellurium from the fraction which would contain the most soluble portion, follow:

	$Te_2O_3(OH)NO_3$.	TeO_2.	Percentage TeO_2.
I.	2.84426	2.37354	83.45
II.	2.55736	2.13397	83.44

The analysis of the nitrate from the fraction which would contain the least soluble portion, was made under the same conditions as before.

	$Te_2O_3(OH)NO_3$.	TeO_2.	Percentage TeO_2.
III.	1.39948	1.16824	83.48
IV.	1.85244	1.54649	83.49

The difference between the average of determinations I and II and the average of III and IV corresponds to a difference of 0.4 in the atomic weight. When a sample weighing 2 grams is used an error of 0.3 mg. in the weight of the nitrate would affect the atomic weight to this extent. Although the weights of the nitrate in the above experiments appear to be accurate to 0.1 mg., nevertheless the difference found is probably more apparent than real.

The basic nitrate is a crystalline compound and may have held mother-liquor within the crystals, although the salt was ground to a fine powder and did not lose weight when heated for ten hours at 120°. On account of this uncertainty, we do not consider the results as data which can be used for calculating the atomic weight of tellurium. The results are of value, however. The analyses of the nitrate prepared from the fractionated tellurium were made under exactly the same conditions, and any error in the method would have affected

the two determinations equally. We can, therefore, safely conclude that the fractionation of potassium bromtellurate did not effect any decomposition of the tellurium, which could be detected by a method capable of giving results accurate to 0.4 of a unit in the atomic weight.

The work described above is preliminary to an atomic weight determination which is now in progress. When a method has been devised which will give accurate results, the atomic weight from the end fractions will be determined, in order to decide whether the difference of 0.4 of a unit indicated by the experiments given above is a real one or not. We hope also to offer more conclusive evidence in regard to the elementary nature of tellurium. The fractional sublimation of tellurium dioxide, which is now in progress, seems to offer a more efficient means of deciding this point than fractional crystallization.

This paper has been published in this unfinished form, as the departure of one of us from the Institute prevents us from continuing the work in common.

BOSTON, Dec. 1, 1899.

XXIV.—THE REDUCTION OF SELENIUM DIOXIDE BY SODIUM THIOSULPHATE.

BY JAMES F. NORRIS AND HENRY FAY.

Some time ago we proposed a volumetric method for the estimation of selenous acid[1] based on the reaction between it and sodium thiosulphate in the presence of hydrochloric acid. The procedure, in brief, is as follows: The solution in which the selenous acid is to be determined is diluted with ice-water, acidified with dilute hydrochloric acid, and an excess of a tenth-normal solution of sodium thiosulphate added. The excess of thiosulphate is determined by titration with a solution of iodine. It was shown that 1 molecule of selenous acid reacted with 4 molecules of sodium thiosulphate, and that the reaction afforded a means for the accurate determination of selenium.

[1] This JOURNAL, **18**, 703.

At the time this method was proposed we were not able to state the exact nature of the reaction, but we have studied further the reduction and are now able to write the complete reaction. The most probable reaction between the two substances may be represented by the following equation:

$$SeO_2 + 4Na_2S_2O_3 = 2Na_2S_4O_6 + Se + 2Na_2O.$$

If strong solutions of selenium dioxide and sodium thiosulphate are mixed, selenium is precipitated, and the solution shows an alkaline reaction. In dilute solutions, on the other hand, no selenium is precipitated, and the reaction is not complete according to the above equation, since the sodium hydroxide formed neutralizes a part of the selenous acid which, accordingly, does not enter into the reaction. If, however, acid is present, 4 molecules of sodium thiosulphate react with 1 molecule of selenium dioxide. The amount of acid required to complete the reaction was determined. This was found to vary with the dilution, the excess of thiosulphate, and the time of reaction. The following table gives the results obtained. In each case 10 cc. of a solution of selenium dioxide, which was equivalent to 26.40 cc. of sodium thiosulphate, according to the ratio $SeO_2 : 4Na_2S_2O_3$, were used:

	Molecules HCl.	$Na_2S_2O_3$ taken. cc.	$Na_2S_2O_3$ used. cc.	Water added. cc.
I.	3	50	17.90	...
II.	4	27	22.02	300
III.	4	27	24.96	300
IV.	4	50	25.40	300
V.	5	30	26.38	300
VI.	4	50	26.40	...

In experiment I., 3 molecules of acid were used and only 17.90 cc. of thiosulphate entered into the reaction. Using 4 molecules in II, 22.02 cc. of thiosulphate reacted. In the third experiment the same proportions were used, but the solutions stood forty minutes before the excess was determined. This had a marked effect on the result, as about 3 cc. more of the thiosulphate reacted. A large excess of thiosulphate hastened the reaction, as is shown in experiment

IV. Experiment V shows that 5 molecules of acid are sufficient at a dilution of 300 cc., and with a slight excess of sodium thiosulphate to complete the reaction. In experiment VI no water was added to the solutions used and the reaction was complete when the proportion of the reagents were $SeO_2 : 4Na_2S_2O_3 : 4HCl$. These are, therefore, the amounts of reagents which enter into the reaction.

In order to determine the products of the reaction, a solution of the constituents in the above proportions was prepared. The study of this solution led to the following equation, which expresses the reaction :

$$SeO_2 + 4Na_2S_2O_3 + 4HCl = Na_2S_4SeO_6 + Na_2S_4O_6 + 4NaCl + 2H_2O.$$

The formation of sodium selenopentathionate, similar to potassium pentathionate, seemed probable, since no selenium was precipitated as a result of the reduction. Debus,[1] in an exhaustive study of Wackenroder's solution, which is prepared by the action of hydrogen sulphide on an aqueous solution of sulphur dioxide, isolated some salts of pentathionic acid in a pure condition, and carefully studied their properties. He gives the following characteristic reactions :

"I. An ammoniacal solution of silver nitrate causes, in a solution of potassic, ammonic, or baric pentathionates, a brown coloration which rapidly becomes darker, and by degrees a black precipitate is thrown down from the mixture. This reaction is not produced in a solution of tri- or tetrathionates, potassic thiosulphate, or ammonic sulphite. An ammoniacal solution of silver nitrate also seems to have no effect on them. Consequently a pentathionate, even if present in very small quantity, can be detected by means of this reaction in a mixture containing potassic tri- and tetrathionates, and sodic, potassic, or ammonic thiosulphates.

"II. Potassic hydroxide, in solutions of pentathionates, immediately produces a separation of sulphur. As tri- and tetrathionates and thiosulphates are not changed by this reagent, a proportionally small quantity of a pentathionate can be detected in a mixture of the four salts by addition of potassic hydroxide.

[1] J. Chem. Soc., **53**, 278.

"III. Ammonia added to a solution of potassic pentathionate causes, after about one or two minutes, a precipitation of sulphur.

"IV. Hydric chloride does not change solutions of tetra- and pentathionates."

A solution prepared by mixing the constituents in the proportions represented in the equation, was subjected to the above tests. A precipitate was formed with ammoniacal silver nitrate, as described above under I, and potassium hydroxide caused an immediate precipitation of selenium. Ammonia acted more slowly, and the solution was stable toward strong hydrochloric acid. The solution showed, therefore, the characteristic reactions of a pentathionate, selenium, however, being precipitated instead of sulphur. This is in accord with the formula proposed, $Na_2S_4SeO_6$. An effort was made to isolate the selenopentathionate, but without success, as selenium was always precipitated when the solutions were concentrated by heat or in a vacuum. From the solution, however, we were able to isolate sodium tetrathionate, which was proved to be such by qualitative and quantitative analysis.

A dilute solution containing the new salt could be boiled some time without change. A number of neutral salts were found to decompose the compound. Stannous chloride caused a precipitation of selenium after a few minutes. A dilute solution of sodium thiosulphate produced the same effect only much more slowly, whereas a number of hours' standing was necessary before potassium iodide caused any decomposition.

An acid solution of tellurium dioxide is reduced by sodium thiosulphate, giving a bright yellow solution, from which sodium hydroxide precipitates tellurium. Tellurium, therefore, probably forms a compound analogous to a selenopentathionate. This is remarkable, since no compounds containing tellurium, analogous to the thionates, are known. Crane[1] attempted to prepare substances similar to the thiosulphates, by boiling sodium tellurite with sulphur, selenium, and tellurium, but there was apparently no reaction.

[1] Dissertation, Johns Hopkins University.

By misunderstanding a statement made in our former paper, Mr. J. T. Norton, Jr.,[1] has been led to study the influence of hydrochcloric acid on titrations with sodium thiosulphate, and to repeat our work on the estimation of selenium. He says, referring to the method, "the explicit statement of the authors that the amount of hydrochloric acid present does not influence the result provided the titration is made at the temperature of melting ice, is so extraordinary in view of generally accepted ideas in regard to the interaction of hydrochloric acid and sodium thiosulphate as to suggest the necessity of a careful investigation of this point." In the paper referred to we made this statement: "It was found necessary to have enough hydrochloric acid present to set free all of the thiosulphuric acid. If the solution is cold a large excess of hydrochloric acid does not affect the titration." Mr. Norton evidently confuses *excess* with *amount*. We used in all of our experiments 10 cc. hydrochloric acid (1.12 sp. gr.), which is seven to eight times the amount required according to the above statement, and obtained excellent results. The statement is, therefore, not so extraordinary as might appear.

As the action of hydrochloric acid on sodium thiosulphate was known to us when we were making a study of the method, we took the precautions to have the solutions containing the acid dilute, and used ice to keep the temperature as low as possible. The necessity for these precautions was stated in the directions given. Mr. Norton further points out that it is advisable to use not more than 20 cc. excess of sodium thiosulphate in order to prevent decomposition by the acid. We have made some new determinations of selenium in order to test the directions given in the original paper under the most unfavorable conditions. The results follow:

	SeO_2 taken. Gram.	$Na_2S_2O_3$ taken. cc.	$Na_2S_2O_3$ used in reaction. cc.	SeO_2 found. Gram.	Dilution. cc.
I	0.0995	43	39.62	0.0995	300
II	0.0336	15	13.39	0.0336	300
III	0.0336	50	13.13	0.0331	300
IV	0.0336	50	13.24	0.0333	300
V	0.0435	50	17.20	0.0432	400
VI	0.0430	50	16.41	0.0412	200

[1] Am. J. Sci., **157**, 287.

In Experiments I. and II. the directions as given in our paper were followed, and a small excess of sodium thiosulphate was used. In order to have a large excess of thiosulphate present in the other experiments, small amounts of selenium dioxide and 50 cc. of thiosulphate were used. In III. and IV. the excess, 36.87 cc., was nearly three times the amount necessary for the reaction—13.13 cc. Since a bare excess only is necessary, a careful analysis would hardly be based on such a procedure. Experiment VI. shows the necessity of working in dilute solutions. In all of the above determinations 10 cc. hydrochloric acid (1.12 sp. gr.) were used, but since 5 cc. is quite sufficient to bring about the reaction, the modification which Mr. Norton suggests as the result of his work, namely the use of the latter amount of acid, can readily be accepted.

Mr. Norton points out also that his results always come high. We had not observed this in our work and accordingly we sought the cause. As we had standardized the sodium thiosulphate by titration against known weights of iodine, under the conditions which were to be used in the subsequent analyses, that is, titration in the cold in the presence of acid, a standardization was made under ordinary conditions. The factor found was higher by about 0.2 per cent than the one previously obtained. This discrepancy was shown to be due to the fact that the iodine-starch reaction is more sensitive at 3° in presence of dilute acids than under the conditions which are ordinarily used in the titration of iodine and thiosulphate. The following table gives the number of cubic centimeters of one-hundredth normal iodine solution required to produce a color with starch under different conditions of temperature and with varying amounts of dilute hydrochloric acid (sp. gr. 1.12). The starch solution was made by grinding 2 grams of soluble starch with 5 cc. of cold water, and pouring the mixture into 500 cc. boiling water. In all tests 5 cc. of this solution were used and diluted to 300 cc. with water.

No.	Acid. cc.	Temperature.	Iodine. cc.
1	....	20°	0.61
2	1.00	20°	0.32
3	10.00	20°	0.26
4	50.00	20°	0.27
5	....	3°	0.30
6	....	15°	0.50
7	....	20°	0.57
8	....	25°	0.85
9	....	30°	1.17
10	10.00	3°	0.15

Experiments 1–4 show the effect of acids and 5–9 the effect of temperature. In Experiment 10 the most favorable conditions for the reaction were combined and 0.15 cc. of the iodine solution gave a distinct color, whereas in the absence of acid, at 25°, 0.85 cc. was necessary. It has long been known that temperature has an effect on the blue compound formed by the action of iodine on starch but, as far as we can find, it has never been shown that this effect is appreciable at the temperatures used in the course of an analysis. Although the error arising is small when the facts brought out by the above experiments are overlooked, nevertheless, when very accurate results are desired, they should be taken into consideration.

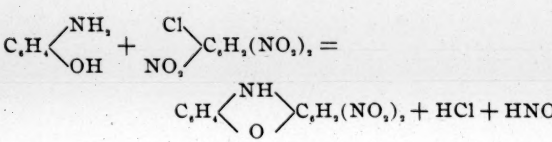
BOSTON, Dec. 1, 1899.

ACTION OF PICRYL CHLORIDE ON PYROCATECHIN IN PRESENCE OF ALKALIES.

BY H. W. HILLYER.

Being engaged in a study of some derivatives of diphenyl ether, $C_6H_5OC_6H_5$, made by the general method of Willgerodt,[1] the attention of the writer was called to the reaction discovered by G. S. Turpin,[2] and used by him in the preparation of dinitrophenoxazine and to the reaction used by F. Kehrmann, in preparing dinitrophenthiazine. Turpin brought together in alcoholic solution one molecular proportion of picryl chloride, one of orthoamidophenol, and two of an alkali. He readily obtained dinitrophenoxazine with the elimination of chlorine, and one nitro group from the picryl chloride as follows:

[1] Ber. d. chem. Ges., **12**, 1278; and **13**, 887. [2] J. Chem. Soc. (London), 1891, 714.
[3] Ber. d. chem. Ges., **32**, 2605.



In this connection the idea came to the writer to ascertain whether a similar reaction would take place on bringing together picryl chloride and pyrocatechin in equimolecular proportions and adding a double molecular proportion of sodium hydroxide, thus forming a double aromatic ether.

Fifteen grams picryl chloride and 6.6 grams pyrocatechin were dissolved in 500 cc. common alcohol and a solution of sodium in alcohol, equivalent to 4.8 grams of sodium hydroxide, were added. The solution turned dark-brown, and after some time deposited a brown precipitate soluble in water. The mixture was heated to 60°–70° for six hours. The brown precipitate gradually disappeared, and was replaced by a dense, yellow, granular precipitate, which, after five hours, did not seem to increase in amount. It was filtered from the solution and washed with alcohol and water, and after drying weighed 13.75 grams, or 85 per cent of the theoretical. The solution filtered from the yellow precipitate contained large quantities of chloride and nitrite.

The crude yellow product melts at 191°–192°.5. It dissolves quite readily in hot benzene, and crystallizes from it on cooling in yellow spherulites. It is best purified by crystallization from hot glacial acetic acid, from which it also separates in lemon-yellow spherulites. By this purification its melting-point is changed but little, the melting-point of the twice crystallized substance being 192°–192°.5. When rapidly heated it decomposes almost explosively, but when carefully heated it may be sublimed in the form of beautiful lemon-yellow leaflets of the same melting-point. It will not dissolve in hydrochloric acid. It dissolves in concentrated sulphuric acid, but apparently separates unchanged on adding water. It will not dissolve except perhaps slightly in dilute alkalies, showing that it is not a phenol. Heated with strong alkalies it dissolves, forming a brown solution, and from this solution

a new substance not yet studied is thrown down on adding an acid.

A portion of the yellow substance twice crystallized from glacial acetic acid, washed with alcohol, and dried for one hour at 130°–140° was analyzed, and gave the following results:

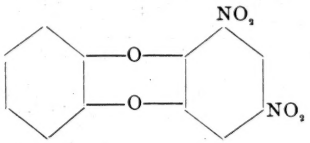
I. 0.2211 gram substance gave 0.4283 gram CO_2, and 0.0486 gram H_2O.

II. 0.2093 gram substance gave 0.4005 gram CO_2, and 0.0431 gram H_2O.

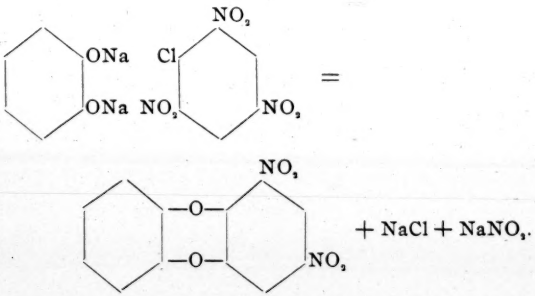
III. 0.2477 gram substance gave 23.2 cc. N at 21° and 748 mm. pressure.

	Calculated for $C_6H_4O_2C_6H_4(NO_2)_2$.	Found. I.	II.
C	52.55	52.83	52.18
H	2.19	2.44	2.29
N	10.22	....	10.49

In view of these analytical results and of the formation of chloride and nitrite in making it, and also from its not being a phenol, the substance may be represented by the formula



and is produced by the reaction



It is a 1,3-dinitroorthodiphenylene dioxide. In view of the stability of the phenyl ethers, it seems probable that the mother-substance of which this is a dinitro derivative may yield other interesting derivatives. For the mother-substance, to indicate its analogy with phenoxazine and phenthiazine, and to point out the presence of the two oxygen atoms connecting the two phenylene groups, the name *phenoxozone* is proposed.

The action by which the new substance, dinitrophenoxozone, is prepared presents one more case of which there are now several in which a nitro group may be split off with formation of a closed chain. The cases published are cases in which the nitro group is in the ortho position to a side chain, usually nitrogenous, and of such a character that it can form either a five-membered or six-membered ring. In the present case there is a formation of a six-membered ring of four carbon atoms and two oxygen atoms.

It is desired to reserve, for study in this laboratory, the action of orthonitrohalogen benzene derivatives on di- and poly-acid phenols of the ortho series, and the character and reactions of the derivatives of diphenylene dioxide or phenoxozone.

LABORATORY OF ORGANIC CHEMISTRY,
UNIVERSITY OF WISCONSIN,
December 20, 1899.

Contributions from the Chemical Laboratory of the Rose Polytechnic Institute.

XVII.—CAMPHORIC ACID.

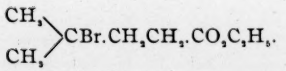
[EIGHTH PAPER.]

BY WILLIAM A. NOYES.

An account of the preliminary work toward the synthesis of 2.33-trimethylcyclopentanone has already been given.[1] The synthesis has now been brought to a successful completion.

Ten grams of sodium were dissolved in 130 cc. of absolute alcohol and 92 grams (calculated 76.5 grams) of methyl malonic ester, $CH_3—CH\begin{matrix}CO_2C_2H_5\\CO_2C_2H_5\end{matrix}$, were added, and then 97 grams of the ethyl ester of γ-bromisocaproic acid,

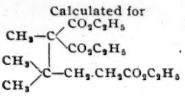
[1] This JOURNAL, **22**, 258.



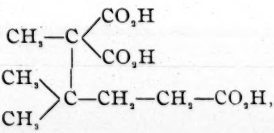
The mixture was boiled for two hours, filtered from sodium bromide, the alcohol distilled over a free flame, the residue filtered again, and then distilled under diminished pressure. After two distillations there were obtained 5 grams of an ester boiling at 180°–187° under a pressure of 20 mm. A second preparation with the use of 121 grams of the brom ester gave 8.1 grams, boiling at 170°–180° under a pressure of 13–15 mm. The portion boiling at 178°–180° was analyzed.

I. 0.1930 gram substance gave 0.4244 gram CO_2, and 0.1404 gram H_2O.

II. 0.2010 gram substance gave 0.4425 gram CO_2, and 0.1473 gram H_2O.

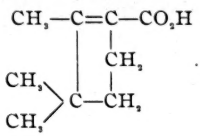
	Calculated for 	Found. I.	II.
C_{16}	60.76	59.97	60.04
H_{28}	8.86	8.08	8.12
O_6	30.38	....	....

The ester was evidently contaminated with some compound or compounds containing less carbon and hydrogen, but, owing to the difficulty of preparation, it could not be further purified. The ester of the first preparation was saponified by boiling for one hour with alcoholic potash. The solution was diluted, evaporated to remove alcohol, acidified, and extracted several times with ether. The impure 2.33-tetramethylhexoic 1,2',6-acid,

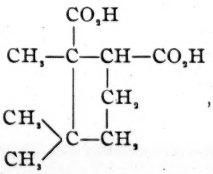


was heated in an oil-bath to 200° for a few minutes till the

evolution of carbon dioxide ceased. The resulting $\alpha\beta\beta$-trimethyladipic acid was mixed with twice its weight of lime and the mixture distilled from a small distilling-bulb. The distillate was distilled and 0.35 gram, which passed over at 160°–180°, was mixed with alcohol and a solution containing 0.6 gram of hydroxylamine chloride and 0.5 gram of sodium hydroxide. After several hours the solution was poured into a crystallizing dish, and allowed to evaporate spontaneously. The oxime which separated was recrystallized from ligroin. It crystallized in needles which melted at 104°. When a small portion was mixed with an equal amount of the oxime prepared from α-hydroxydihydrociscampholytic acid,[1] the mixture melted at exactly the same temperature, and after solidification the melting-point still remained the same. The identity of the two substances is, therefore, established, and the ketone from camphor is 2.33-trimethylcyclopentanone. From this it follows that ciscampholytic acid is the Δ^1-2.33,-trimethylcyclopentenoic acid,

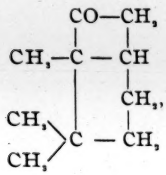


There also remains no reasonable doubt that Perkins'[2] older formula for camphoric acid,



and Bouveault's[3] formula for camphor,

[1] This JOURNAL, **22**, 265.
[2] Proc. Chem. Soc., 1896, 191.
[3] Chem. Ztg., **21**, 762.



are correct.

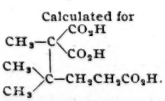
Owing to the small quantity of the oxime available, the analysis was not satisfactory.

0.0353 gram substance gave 0.0387 gram of nitrogen.

	Calculated for $C_8H_{14}NOH$.	Found.
N	9.93	10.96

The ester from the second preparation above was saponified by longer boiling with alcoholic potash, and there was obtained from it an acid which partly solidified. By treatment with a small amount of ether the pure 2.33-tetramethylhexanoic 1,2[1],6-acid was obtained. The acid crystallizes from ether in needles. When heated it begins to decompose at about 175°, but does not melt to a clear liquid till a somewhat higher temperature is reached. When heated to 190°–200° for a few minutes it is decomposed quantitatively into carbon dioxide and $\alpha\beta\beta$-trimethyladipic acid. The ammoniacal solution of the acid gives no precipitate with calcium chloride in the cold, but, on warming, a precipitate is formed, which redissolves on cooling.

0.1226 gram of the acid gave 0.2319 gram CO_2, and 0.0780 gram H_2O.

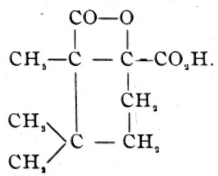
	Calculated for 	Found.
C_{10}	51.72	51.59
H_{16}	6.90	7.07
O_4	....	....

0.65 gram of the pure trimethyladipic acid obtained by heating a portion of the acid last mentioned to 200° was mixed with 2 grams of lime and the mixture distilled from a small

distilling-bulb. The decomposition took place with very little blackening and a light-yellow oil passed over. This had the peculiar peppermint, musty odor, characteristic of the 2.33-trimethylcyclopentanone from camphor. It was partly purified by distilling with steam, and an attempt was made to prepare the condensation-product[1] with benzaldehyde. The condensation took place easily, but a viscous oil was formed from which no crystals could be obtained. Unfortunately, none of the condensation-product from the preparation from camphor remained with which to start the crystallization. While the failure to secure the crystallized condensation-product is disappointing, it cannot be considered that it throws any doubt on the positive result obtained with the oxime.

The demonstration of the correctness of Perkins' older formula for camphoric acid and of Bouveault's formula for camphor, which has been furnished above, renders it possible to discuss, with some degree of certainty, the transformations which these bodies undergo. Only a few points will be taken up for consideration in the present paper.

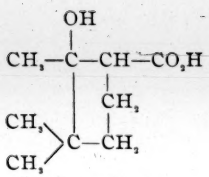
Blanc has recently[2] expressed the opinion that camphanic acid is a β-lactone having the structure,



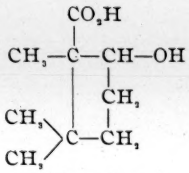
The formation of this acid from bromcamphoric anhydride appears to furnish a strong basis for this view. In the opinion of the writer, however, it appears more probable that the acid in question is a normal γ-lactone, and for the following reasons:

Neither of the β-hydroxy acids formulated below gives a lactone directly.

[1] This JOURNAL, **22**, 265.
[2] Bull. Soc. Chim., **19**, 353.



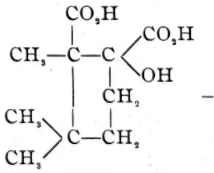
β-Hydroxydihydrocampholytic acid.[1]



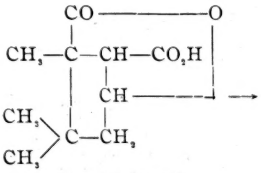
β-Hydroxylauronic acid.[2]

Further, camphanic acid loses carbon dioxide and gives campholactone and lauronolic acid[3] on distillation. Campholactone is also formed on warming γ-lauronolic acid with dilute sulphuric acid.[4] γ-Lauronolic acid must be a βγ-unsaturated acid (see below) and the formation of a β-lactone from it is highly improbable.

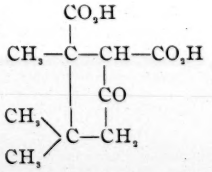
The consideration of camphanic acid as a γ-lactone also furnishes a much more satisfactory explanation of the formation of camphoronic acid from camphoric and camphanic acids than if we consider it a β-lactone. The steps appear to be as follows: the transformation of the first oxidation-product to camphanic acid being accomplished by the elimination, addition, and a second elimination of water. Such transformations take place with peculiar ease in this series :

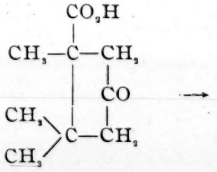


First oxidation-product.

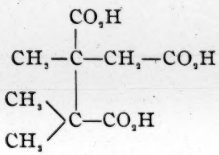


Camphanic acid.



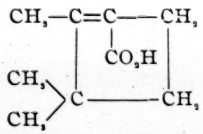


[1] This JOURNAL, **17**, 424.
[2] *Ibid.*, **18**, 687.
[3] Ann. Chem. (Liebig), **227**, 10.
[4] This JOURNAL, **17**, 433.

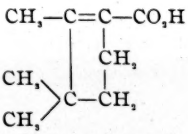


Camphoronic acid.

In a previous paper[1] the opinion has been expressed that the "cistrans"-campholytic acid and ciscampholytic acid are stereomeric. In the light of our present knowledge the two acids would be formulated thus:



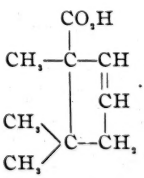
Cistranscampholytic acid.



Ciscampholytic acid.

While the formula for cistranscampholytic acid here given is not considered as established, it appears to be more in accordance with the facts now known than that given by Blanc,[2] who considers the acid to be a $\beta\gamma$-unsaturated acid.

Lauronolic and γ-lauronolic acids, apparently, have each the formula

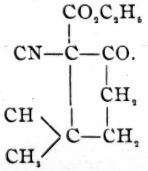


Such an acid is optically active, and it is possible that γ-lauronolic acid is one of the optical isomers, and that lauronolic acid is the racemic form. It is my purpose to undertake, as soon as possible, a systematic study of these four acids with the hope of clearing up their relationships.

[1] This JOURNAL, 17, 423.

[2] Private communication.

It has been found that when the sodium derivative of the methyl ester of cyanacetic acid acts on the ethyl ester of γ-bromisocaproic acid the same dimethylcyancarboxethylcyclopentanone described in my last paper,[1] is formed. The melting-point of the product is the same, and the analysis gave 6.79 per cent of nitrogen. Calculated 6.70 per cent. The structure of the substance is, therefore,



It is hoped that the synthesis of camphoric acid, itself, may be effected with the aid of this compound.

TERRE HAUTE, Dec. 19, 1899.

Contributions from the Sheffield Laboratory of Yale University.

LXXIII.—ON THE REARRANGEMENT OF IMIDO-ESTERS.

[SECOND PAPER.]

BY HENRY L. WHEELER.

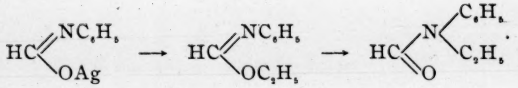
As described in our[2] first paper on this subject, we had occasion to prepare phenylformimidoethyl ester, and, instead of following the usual method[3] of treating silver formanilide with ethyl iodide at low temperatures, we heated the materials in a closed tube to 100°. We thereupon unexpectedly obtained a rearrangement of phenylformimidoethyl ester into the isomeric ethyl anilide :[4]

1 This JOURNAL, **22**, 260.

2 Wheeler and Johnson : This JOURNAL, **21**, 185.

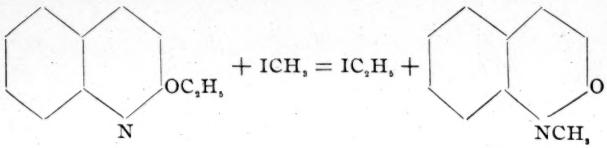
3 Comstock : This JOURNAL, **13**, 514.

4 The prediction of Freer and Sherman in regard to this salt is now completely fulfilled, *i. e.*, "With suitable alkyl or acyl halides and alteration of conditions, it will probably be possible to procure both oxy and nitrogen derivatives from the silver salt" (This JOURNAL, **18**, 571). In This JOURNAL, **18**, 381, Wheeler and Boltwood showed that this salt gives in fact benzoylformanilide, a nitrogen derivative, with benzoyl chloride.



This was confirmed by the fact that benzimidoethyl ester gave ethylbenzamide when heated with ethyl iodide. We stated that we hoped to reserve the further examination of this rearrangement for this laboratory.

On the publication of these results Professor Knorr called our attention to his work along similar lines in the case of the cycloimido esters. He had previously shown that the oxygen esters of the α-quinolones[4] are converted by methyl iodide "langsam schon in der Kälte, rasch und vollständig in der Wärme, in die Stickstoff-Methylester." Thus, ethoxyquinoline is converted into methylquinolone :



He also found that the oxygen methyl and ethyl esters of oxy-γ-lepidine behaved in a similar manner. He showed that this reaction in the case of γ-methoxyquinaldine[2] takes place first by addition ; and that this intermediate product then when heated to 200° gives the nitrogen derivative. Again, along with E. Fertig,[3] he found that α-phenyl-γ-methoxyquinoline was converted directly into the isomeric derivative with methyl iodide, and finally he stated : "Ich hoffe bald weitere Mittheilung machen zu können, ob sich ganz allgemein die Imidoäther R'N : CR''OR''' durch Jodmethyl in Amide secundärer Basen, $CH_3R'NCR''O$ überführen lassen."

In view, however, of the work already done in this laboratory, and, since I informed Professor Knorr of my desire to publish the work of my students, which was finished at the time our first publication appeared, Professor Knorr kindly gave over the entire field to me.

[1] Ber. d. chem. Ges., **30**, 929.
[2] *Ibid.*, **30**, 924, 926.
[3] *Ibid.*, **30**, 937.

I wish to take advantage of this occasion to thank him for his kindness and also to refer to other work bearing on the rearrangement of the imido esters.

In the year 1885 Ponomarew[1] found that by treating silver cyanurate with alkyl iodides, at low temperatures, the oxygen esters result, while at higher temperatures the nitrogen esters are the chief products.

In 1886 Hofmann[2] showed that the oxygen methyl ester of cyanuric acid is transformed into the nitrogen ester simply by heating.

In 1891 Andreocci[3] found that when phenylpyrodiazolon or phenylmethylpyrodiazolon is methylated, and then treated with methyl iodide, similar results are obtained, and that the oxygen methyl compounds, when heated to 200°, are also transformed into the nitrogen compounds.

All the above are examples of the rearrangement of cycloimido esters. The transformation of benzimidochlorethyl ester into β-chlorethylbenzamide, under the influence of heat alone, as described by Gabriel and Neumann,[4] is especially interesting, and, outside of our work, this appears to be the only known example of a rearrangement taking place in the acyclic series.[5]

In the cycloimido ester series N-alkyl derivatives have frequently been obtained from silver salts, but particularly at higher temperatures. This has notably been the case in the uric acid group in Fischer's investigations.[6] Since, however, the silver salt of hydroxycaffeïn gives with ethyl iodide chiefly ethoxycaffeïn, he concludes that the former substance does not have the grouping —CO—NH, but —COH=N—. In this case he also noticed the formation of some tetramethyluric acid.

1 Ber. d. chem. Ges., **18**, 3271.

2 *Ibid.*, **19**, 2061.

3 *Ibid.*, **24**, R, 203.

4 *Ibid.*, **25**, 2383.

5 I wish to express my thanks to Professor Gabriel for calling my attention to this work. In a private communication from Dr. Stieglitz the following was mentioned: "I intended calling your attention to Knorr's paper in the Berichte, 1897, pp. 929–933. At the time when this came out I was heating ethyl imidobenzoate in a sealed tube at 100° with ethyl iodide, but did not go on with the action on account of Knorr's reservation."

6 Ber. d. chem. Ges., **30**, 550.

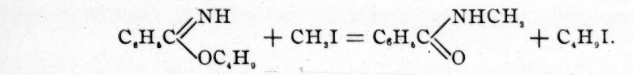
We find that the imidoesters of Pinner react slowly, even at ordinary temperatures with methyl and ethyl iodides giving alkyl amides. In the case of the benzimido esters benzamide and benzonitril invariably accompany the alkyl amide. In the lower-boiling portions of the reaction-product the presence, in small amount, of a substance that gave off an amine odor on distilling was also observed.

With isobutyl iodide the chief products were benzamide and isobutylene:

$$C_4H_9I = C_4H_8 + HI,$$

and $C_6H_5C(NH)OC_4H_9 + HI = C_6H_5CO.NH_2 + C_4H_9I.$

In general, however, the chief reaction of methyl and ethyl iodides is as follows:



In the case of the action of ethyl iodide on benzimidoethyl ester, diethylbenzamide was sought for, but no evidence of its presence was observed.

Besides others there are, therefore, three principal reactions that take place when the acyclic imidoesters are treated with the lower alkyl iodides:

a. A transference of alkyl group from oxygen to nitrogen.

b. The formation of hydrogen iodide which with unaltered imidoester gives a primary amide (benzamide).

c. A decomposition of the imidoester into nitril and alcohol.

Experiments with Benzimidoesters.[1]

Benzimidomethylester and methyl iodide readily react at ordinary temperature. Thirty grams of the imidoester were allowed to stand for a month with 16 grams of methyl iodide (0.5 molecule); in a short time crystals separated, which finally developed into well-crystallized, flattened prisms. This material proved to be benzamide containing a small amount of cyanphenin and it weighed 3.5 grams. The oil filtered from this was distilled at 13-12 mm. pressure (*A* below).

For comparison, 20 grams of the ester were heated to about

[1] The imidoesters in the following experiments were all freshly distilled. Under diminished pressure they boil unaltered without exception.

100° for five and a half hours with 1 gram of methyl iodide. On cooling, crystals separated but were not filtered off, the whole being distilled at 9–12 mm. pressure when the following fractions were obtained (*B*) :

A.		*B.*	
	Grams.		Grams.
(1) below 159°	3.4	(1) below 155°	2.9
(2) 159°–169°	9.8	(2) 155°–165°	7.9
(3) 169°–174°	11.5	(3) 165°–168°	7.7

The first portions, in both cases, consisted chiefly of benzonitril.

The second portions did not solidify on standing or when cooled in a freezing-mixture. When distilled at 760 mm. pressure, 2-*B*, for example, began to boil at 276°, and a strong odor of amine and benzonitril was given off. The material had no constant boiling-point, but distilled steadily up to 291°, when the distillation was stopped and the residue (the greater portion) was cooled. It then solidified and, when crystallized from a small amount of alcohol, gave colorless flattened prisms melting at 82°. This material had all the properties of methylbenzamide (see below).

The third fractions in both cases readily solidified and were crystallized from water. 3-*A* gave square tables of methylbenzamide, while 3-*B*, from which benzamide was not removed by filtration, gave a mass of plates melting at 128°, *i. e.*, benzamide.[1]

The products identified in these reactions are, therefore, methylbenzamide, benzamide, benzonitril, and a trace of cyanphenin.

From the above it appears that the action of methyl iodide on benzimidomethyl ester is the same at 100° as at ordinary temperatures, and that a small amount of methyl iodide produces practically the same result in this reaction as a large amount.

[1] In describing benzimidomethyl ester (This JOURNAL, **17**, 398), the author stated that this ester, on standing, deposits benzamide. It is now known that this result was due to the presence of methyl iodide since the pure ester prepared by Pinner's method does not deposit benzamide on standing. Dains (J. Am. Chem. Soc., **21**, 166), in his work on the isoureas, quotes this supposed behavior in his comparisons. Benzimidomethyl ester, when pure, is quite stable.

Benzimidoethyl Ester and Ethyl Iodide.—In the previous paper the ester was heated with ethyl iodide, while the following is a description of the action at ordinary temperatures: 49 grams of the ester were mixed with 52 grams of ethyl iodide and allowed to stand for a month. At the end of this time 5.2 grams of beautifully crystallized cyanphenin separated. It melted sharply from 230°–231°. The filtrate from this was distilled at 773 mm. pressure, when 51.7 grams of crude ethyl iodide were recovered (below 185°). After the ethyl iodide was over, the material began to distil at 185° when, up to 278°, 2 grams of fishy-smelling oil were obtained, mostly benzonitril. From 278°–293° 10.8 grams of oil were collected, while from 293°–300° the remainder practically all came over. This weighed 23.5 grams, and when crystallized once from dilute alcohol it separated in small flattened prisms and melted from 69°–70°, this material being pure ethylbenzamide.

A search was made for diethylbenzamide in the portion boiling from 278°–293°, it having been found that this substance boils at 282°. For this purpose the fraction was cooled in a freezing-mixture, and considerable ethylbenzamide was then removed by filtering. The filtrate, when distilled at 763 mm. pressure, gave a few drops of fishy-smelling oil below 200°; then up to 290° no definite boiling-point was observed, the mercury in the thermometer not stopping an instant at the boiling-point of diethylbenzamide. From the lower-boiling portion of this fraction benzonitril was obtained; the higher consisted mostly of benzamide.

The chief products of this reaction are, therefore, ethylbenzamide, benzamide, benzonitril, and cyanphenin.

Diethylbenzamide was prepared from 5 grams of diethylamine by means of the Baumann-Schotten reaction. It was obtained as a clear, colorless oil that became thick, but did not solidify at —25°. It boiled from 282°–283° at 763 mm. pressure, and agreed in properties with the products obtained by Hallmann[1] and by Romburgh.[2] It is less soluble in warm water than in cold.

[1] Ber. d. chem. Ges., **9**, 846.
[2] Recueil d. Travaux chim. d. Pays-Bas., **4**, 387.

An experiment to determine whether benzonitril, ethyl iodide, and ethyl alcohol react under the above conditions was performed as follows: 10.5 grams of benzonitril were mixed with alcohol and ethyl iodide in molecular proportions and the mixture heated from 100°–115° for nine hours. On opening the tube there was no pressure, and, on distilling at about 10 mm. pressure, the entire material boiled from 71°–72° (benzonitril), except a few drops of black tar which remained in the residue. No benzamide or ethylbenzamide was formed.

Benzimidoisobutyl Ester and Methyl Iodide.—Thirty grams of the ester were heated with a little over one molecular proportion of methyl iodide from 80°–115° for four hours. On cooling, an oil was obtained containing some crystals in suspension. They were filtered and consisted of cyanphenin and benzamide (separated by boiling water). The oil was distilled at 765 mm. pressure, when the portion boiling below 160° was collected. It weighed 24 grams, while the calculated yield of isobutyl iodide is 31 grams. On redistilling, it boiled mostly from 121°–121°.5, and proved to be pure isobutyl iodide.

The residue boiling above 160° was then distilled at 18–19 mm. pressure, when three fractions were obtained: (1) 98°–172° (benzonitril); (2) 172°–177°; (3) 177°–187°. The last portion readily solidified; the second deposited crystals on standing. On crystallizing the material from alcohol prisms were obtained melting at 82°. Romburgh gives 78° as the melting-point of methylbenzamide. That the material is methylbenzamide is shown by its properties and the following nitrogen determination:

	Calculated for C_8H_9NO.	Found.
N	10.37	10.40

The most striking property of the alkylbenzamides is the behavior of their saturated aqueous solutions. When these are warmed they become turbid in consequence of the separation of the amides in the form of oils. This turbidity disappears again on warming to boiling, and on again cooling, this behavior is reversed.

Benzimidoisobutyl Ester and Isobutyl Iodide.—Thirty grams of the former were heated from 165°–185° for several hours. On cooling and opening the tube considerable inflammable gas escaped. It was concluded from its odor that this was isobutylene. On distilling, 21 grams of isobutyl iodide were recovered. The remaining material was distilled at 13 mm. pressure, when benzonitril and benzamide were the chief products. The higher-boiling portion was crystallized from water, when it melted from 126°–127°, and a nitrogen determination gave:

	Calculated for $C_6H_5CO.NH_2$.	Found.
N	11.57	11.22

Isobutylbenzamide.—This was prepared from 6 grams of isobutylamine by the Baumann-Schotten method. The material thus prepared boiled from 173°–178° at 13 mm. pressure, and at 308°–313°, with slight decomposition, at 760 mm. pressure. The oil thus obtained solidified to a beautiful crystalline mass, which was crystallized from alcohol with the aid of a freezing-mixture. It then melted at from 57°–58°. A nitrogen determination gave:

	Calculated for $C_{11}H_{15}NO$.	Found.
N	7.91	8.19

Isobutylbenzamide forms chisel-shaped prisms and is difficultly soluble in water and petroleum ether, readily in ether, chloroform, and alcohol.

Benzimidoethyl ester and isobutyl iodide did not act smoothly. The products obtained were benzamide, benzonitril, cyanphenin, ethyl and isobutyl benzamides, and a substance, in too small amount for identification, which, after crystallization from alcohol separated in colorless, stout crystals, which melted at 192° with effervescence.

EXPERIMENTS WITH PHENYLACETIMIDOESTERS.

By Treat B. Johnson.

Phenylacetimidomethyl Ester and Methyl Iodide.—(1) Twenty grams of phenylacetimidomethyl ester were heated with 9.5 grams of methyl iodide (1 molecule of ester to 0.5 molecule of iodide) for an hour from 95°–105°. The product was then di-

luted with ether and the precipitated material filtered off. This proved to be phenylacetamide, and weighed 2.2 grams. The ether solution was evaporated and the oil distilled at 25–28 mm. pressure. The first fraction was collected from 115°–to 187°. This weighed 4.2 grams and consisted mostly of phenylacetonitril. The second fraction was collected from 187°–197°. This weighed 6 grams and was crude methylphenylacetamide containing phenylacetamide. On crystallizing it from benzene and ligroin it melted at 147°, and on recrystallizing it from water it melted from 154°–155° (the melting-point of phenylacetamide). If, however, the higher-boiling fractions are crystallized from alcohol by means of a freezing-mixture methylphenylacetamide is obtained.

(2) For comparison, 20 grams of phenylacetimidomethyl ester were again heated, this time with only 0.6 gram of methyl iodide for six hours to the same temperature as before. The residue left by ether (phenylacetamide) weighed 2.7 grams. On distilling the remainder at 27 mm. pressure the first fraction, boiling between 110°–187°, weighed 4.8 grams; the second fraction, 187°–197°, weighed 5.5 grams.

(3) In another experiment 30 grams of the ester were heated with 14.2 grams of methyl iodide, for six hours, from 100°–110°. In this case the phenylacetamide weighed 3.6 grams. The first fraction of the oil distilled at about 20 mm. pressure, boiled at from 110°–180° (mostly 110°–130°), and weighed 8.4 grams; the second fraction (184°–190° at 18 mm. pressure) weighed 10.5 grams. This latter was combined with the second fraction obtained in our second experiment and redistilled at 19 mm. pressure, when the greater portion boiled from 179°–184°, leaving little or no residue. This distillate readily solidified and, when crystallized from alcohol, finally melted from 54°–57° (the melting-point of methylphenylacetamide is given by Taverne[1] as 58°).

A nitrogen determination in this material gave:

	Calculated for $C_6H_5CH_2CONHCH_3$.	Found.
N	9.39	9.14

The substance formed in chief amount in these reactions is, therefore, methylphenylacetamide.

[1] Recueil d. Travaux chim. d. Pays-Bas., **16**, 35.

In order to simplify the comparison, the above results are given in the following table:

	Grams of ester taken.	Weight of iodide.	Time.	Weight of phenyl-acetamide. (*b*)	Weight of first fractions. Crude nitril. (*c*)	Weight of second fractions. Crude methyl amide. (*a*)
(1)	20	9.5	1 hr.	2.2	4.2	6.0
(2)	20	0.6	6 hrs.	2.7	4.8	5.5
(3)	30	14.2	6 hrs.	3.6	8.4	10.5

From this it is evident that, in this rearrangement the same result is obtained whether a little (0.6 gram) or a large amount (9.5 grams) of alkyl iodide is used. The close agreement of experiments (1) and (2) under widely different conditions suggest that there is some definite relation between the three principal reactions mentioned in the introduction. The columns (*a*, *b*, *c*) show roughly to what extent these three reactions take place. In estimating this, however, it must be remembered that the total weight of phenylacetamide is low according to column (*b*); that the weight of nitril includes some phenyl- and some methylphenylacetamide; and that column (*a*) represents a mixture of the latter two substances.

Phenylacetimidoethyl Ester and Ethyl Iodide.—Twenty grams of the ester were heated from 100°–106° with 19.1 grams of iodide for six hours. On cooling, the tube contained a thick, red oil, together with some plates. The contents of the tube were extracted with ether, and the insoluble residue, after being crystallized from water, melted from 153°–154°; this was pure phenylacetamide. The ether was then evaporated and the remaining oil was distilled at 13 mm. pressure. The first fraction, collected below 178°, proved to be chiefly phenylacetonitril. The second fraction, collected from 188°–198° at 17 mm. pressure, was obtained as a thick oil which soon solidified in a freezing-mixture. This, when crystallized twice from water, separated in the form of colorless plates melting from 73°–74°. A nitrogen determination shows that this material is ethylphenylacetamide:

	Calculated for $C_6H_5CH_2CONHC_2H_5$.	Found.
N	8.58	8.45

In this rearrangement, in certain cases, some high-boiling material was formed, but this decomposition-product was not examined.

(2) 34.8 grams of phenylacetimidoethyl ester were heated with 33.3 grams of ethyl iodide (1 molecule of ester to 1 molecule of iodide) for six hours from 95°–106°. The amount of phenylacetamide then obtained, on proceeding as above, weighed 2.5 grams, and the amount of crude ethylphenylacetamide weighed 10.9 grams, the remainder being phenylacetonitril and some high-boiling residue.

(3) In another experiment 20 grams of the ester were heated to 100°–110° for six hours with 19.1 grams of ethyl iodide, when the amount of amide isolated weighed 1.3 grams, and the amount of crude ethylamide weighed 5.2 grams.

In all of the above experiments the first fractions were tested for unaltered imidoester by mixing a portion with benzene, and passing in dry hydrogen chloride, when no precipitate was produced; hence in each case the imidoester had entered into reaction completely.

EXPERIMENTS WITH FURIMIDOMETHYL ESTER, *p*-TOLENYLIMIDOMETHYL ESTER, AND *β*-NAPHTHYLIMIDOETHYL ESTER.

BY MUNSON D. ATWATER.

Furimidomethyl ester, $C_4H_3O.C\begin{matrix}NH\\ \diagdown\\ OCH_3\end{matrix}$, was easily obtained from furyl cyanide by following the directions of Pinner[1] for the preparation of the corresponding ethyl ester. It was obtained as a clear, colorless oil of peculiar odor. When distilled at 8 mm. pressure it boiled from 52°-57°. Redistilled at 762 mm. pressure it boiled from 169°–172°; and a nitrogen determination gave the following result:

	Calculated for $C_6H_7NO_2$.	Found.
N	11.2	11.4

Furimidomethyl Ester and Methyl Iodide.—(1) Nineteen grams of the ester were heated for six hours at 100° with a little over 10 grams of methyl iodide. The product, a light-yellow oil,

[1] Die Imidoäther, p. 50.

was distilled at 21 mm. pressure, when 12 grams of material, boiling from 137°–147°, was obtained. This was redistilled at ordinary pressure and collected between 250°–253°. This portion, on standing several days in a desiccator, deposited a considerable crop of colorless, stout crystals, which, when crystallized from ligroin, melted at 64°. A nitrogen determination gave :

	Calculated for $C_8H_7NO_2$.	Found.
N	11.2	11.4

This material is, therefore, methylpyromucamide. The corresponding ethylpyromucamide was found by Wallach[1] to be an oil boiling at 258°.

(2) In another experiment 30 grams of the imidoester were mixed with 17 grams of methyl iodide and allowed to stand nineteen days. At the end of this time 1 gram of pyromucamide had separated, melting at 140°. The oil filtered from this was distilled at 20 mm. pressure. The oil collected below 143° had the odor of the unaltered material, while the remaining portion, between 143°–148°, solidified and proved to be a mixture of pyromucamide and methylpyromucamide.

The behavior of this ester with methyl iodide is therefore closely similar to that of the preceding.

p-Tolenylimidomethyl Ester.—This ester was prepared from *p*-tolunitril by Pinner's directions. It was obtained as a clear, colorless oil, with an odor entirely different from that of the nitril. It boiled at 105°.5 at 10.5 mm. pressure. A nitrogen determination gave :

	Calculated for $C_9H_{11}NO$.	Found.
N	9.39	9.48

p-Tolenylimidomethyl Ester and Methyl Iodide.—Twenty grams of the ester were heated to 100° for four hours. A little pressure was found on opening the tube, which was filled with a yellow crystalline mass of material. On crystallizing twice from water(?) this melted from 144°–145° (the melting-point of *p*-toluic methylamide is given by Gattermann and Schmidt[2] as 143°). A nitrogen determination gave :

[1] Ann. Chem. (Liebig), **214**, 229.
[2] *Ibid.*, **244**, 51.

	Calculated for $C_9H_{11}NO$.	Found.
N	9.39	9.36

p-Tolenylimidomethyl Ester and Methyl Alcohol.—Fifteen grams of the ester were heated with one molecular proportion of methyl alcohol for six hours at from 100°–110°. As there appeared to be no reaction, the mixture was heated at from 100°–140° for six hours more, and finally at from 150°–175° for some time. The material then had the odor of nitril, and it was distilled at 13 mm. pressure, when, after the alcohol escaped, it all boiled from 95°–97° (the boiling-point of *p*-tolunitril), except a very slight residue. This, crystallized from water, melted at 159°, and was therefore *p*-toluic amide. Under these conditions no rearrangement took place.

β-Naphthylimidoethyl Ester and Ethyl Iodide.—The ester was prepared from β-naphthonitril, Pinner's directions being followed. It was found that it could be distilled under diminished pressure, but the record of its boiling-point is not at present available to the writer. That it did not suffer decomposition in this treatment is shown by the following nitrogen determination :

	Calculated for $C_{13}H_{13}NO$.	Found.
N	7.0	7.4

The material thus prepared is a clear, colorless oil, and quite stable. Twenty-four grams of this ester were heated with 9.4 grams of ethyl iodide for six hours at 100°. On cooling, the tube was found to contain a solid mass of yellow material. It was treated with alcohol, which left behind a small amount of white crystals which melted above 280°. The soluble part, when crystallized from alcohol, melted constantly at 129°–131°, and is undoubtedly ethyl-β-naphthamide, but a nitrogen determination gave 8.1 per cent of nitrogen. (Calculated for amide 8.2 per cent, for ethyl amide 7.0 per cent.) The lack of sufficient pure material prevented a duplicate analysis.

EXPERIMENTS WITH SILVER SUCCINIMIDE AND BENZOYL-BENZIMIDOETHYL ESTER.

By Bayard Barnes.

Silver Succinimide and Methyl Iodide.—It was shown by Comstock and Wheeler[1] that if perfectly dry silver succinimide is treated with alkyl iodides at ordinary temperatures, and especial care is taken to avoid moisture, oxygen esters can be isolated. The formation of a small amount of the nitrogen ester under these conditions was also observed, and it was remarked that "If the nitrogen ether is formed by molecular rearrangement from the oxygen ether that rearrangement must take place in this case at ordinary temperature." This we now know to be the case, since this rearrangement is the chief reaction at high temperatures. For example: 27 grams of the silver salt were heated with 22.8 grams of methyl iodide for six hours at 100°. The material was then extracted with ether and distilled at 20 mm. pressure, when it boiled from 140°–155°. This readily solidified and, on crystallizing from alcohol, it melted from 68°–70°. A nitrogen determination gave:

	Calculated for $C_5H_7NO_2$.	Found.
N	12.38	12.45

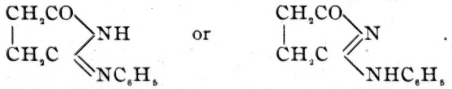
The material is therefore *N*-methylsuccinimide. On extracting the silver residue with alcohol, and crystallizing the extract from benzene, succinimide was obtained.

Silver Succinimide and Ethyl Iodide.—(1) Twenty-four grams of the silver salt and 22.5 grams of ethyl iodide were heated for twelve hours at 100°. As unaltered silver salt still remained, 13.8 grams more iodide were added, and the whole reheated six hours longer. The material was then extracted with benzene and distilled at 20 mm. pressure. The first fraction was collected between 122°–132°; the second from 132°–142°; while above 142° the material solidified in the delivery tube.

The first portion was a pale-yellow oil at ordinary temperature, but it solidified on cooling, and, on freezing out of ether,

[1] This Journal, 13, 519.

it was obtained in colorless crystals melting at 26° (the melting-point of *N*-ethylsuccinimide). The second fraction was mixed with a little aniline, and the presence of the oxygen ethyl ester established by the formation of crystals, which, after purification by dissolving in hydrochloric acid and precipitating with ammonia, melted at 216°, this substance being the "base" described by Comstock and Wheeler, which perhaps may be called α-ketopyrrolidine-α-phenylimide or α-anilidopyrrolon according to whether it has the structure :



The third fraction or residue was found to consist of succinimide.

(2) In another experiment 30 grams of the silver salt were heated with 45 grams of ethyl iodide for ten hours at from 150°–155°. The material was then extracted with dry chloroform and the extract distilled at about 20 mm.(?) pressure. The portion boiling below 134° was redistilled at ordinary pressure, when it nearly all came over at from 233°–235° (*N*-ethylsuccinimide boils from 234°–235°). A nitrogen determination in this material gave :

	Calculated for $C_6H_9NO_2$.	Found.
N	11.02	10.70

It follows from the above that the oxygen ethers of succinimide undergo rearrangement at high temperatures with methyl and ethyl iodides giving the isomeric nitrogen compounds.

Benzoylbenzimido Ester and Ethyl Iodide.—As an example of the behavior of the acylimido esters with ethyl iodide, we describe the following experiment. We were unable to discover any evidence of a rearrangement taking place in this case. This is probably due to the negative character of the acyl ester rather than to a stereochemical interference depending on the molecular magnitude of the =NR grouping. This subject will be investigated later.

Twenty grams of benzoylbenzimidoethyl ester and 6 grams of ethyl iodide were heated for eight hours at from 110°–120°, when the material was found to be unaltered. It was reheated for seven hours at from 120°–150° with the same result. Finally, when heated to 200° for six hours, it decomposed. On opening the tube there was considerable pressure and a strong odor of benzonitril. The material was shaken with sodium carbonate and extracted with ether. The solution of sodium carbonate extracted benzoic acid, and the ether took up benzonitril and ethyl benzoate. The amount of benzonitril obtained weighed 5.6 grams, while the calculated yield of benzonitril for the following decomposition is 8 grams:

$$C_6H_5C\begin{cases}N\,COC_6H_5\\ OC_2H_5\end{cases} = C_6H_5CN + C_6H_5COOC_2H_5.$$

It is our intention to continue the study of these rearrangements in other series.

NEW HAVEN, CONN., June 27, 1899.

THE DOUBLE HALIDES OF ANTIMONY WITH ANILINE AND THE TOLUIDINES.

BY HOWARD H. HIGBEE.[1]

This investigation, like others in the series, was undertaken for the purpose of testing the truth of the laws governing the composition of double halides first pointed out by Professor Remsen.[2]

The method of preparing the salts was to bring the halide of the base together with the corresponding halide of antimony, each constituent being previously dissolved in the corresponding halogen acid.

The results were found to be most satisfactory when each solution was heated before mixing; the base was then added to the metallic chloride.

[1] From the author's dissertation submitted to the Board of University Studies of the Johns Hopkins University, June, 1896, for the degree of Doctor of Philosophy. The investigation was undertaken at the suggestion of Professor Remsen and was carried on under his guidance.

[2] This JOURNAL, **11**, 291; and **14**, 87.

The plan adopted in making the mixtures was to add the halide of the metal in gradually increasing molecular proportions to 1 molecule of the halide of the base.

Since in no case the analyses of any of the mixtures indicated that more than 1 molecule of the halide of the metal had combined with 1 molecule of the halide of the base, mixtures were not made containing more than 3 molecules of the halide of the metal to one molecule of the halide of the base.

Similar trials were then made in the other direction, *i. e.*, 1 molecule of the metallic halide was mixed with a gradually increasing number of molecules of the halide of the organic base in the ratios of 1 : 2, 1 : 3, 1 : 4, and 1 : 6, respectively. The limit of double salt formation in this direction was considered reached, since in many cases the halide of the base crystallized out even in mixtures of 1 : 3, and in no case was a salt found which contained more than 4 molecules of the halide of the base to one of the antimony.

Every mixture made produced a double salt of some kind. When the solutions were of a proper consistency the formation of the crystals was of a uniform character, and they were easily obtained, as a rule, in that condition. The compounds formed differed markedly in their powers of crystallization, but as the formation of crystals with well-defined angles and faces would require days and often weeks, no special attempt was made to gather and study the substances crystallographically. Such investigation was further interfered with by the fact that many of the substances rapidly underwent changes which rendered them unfit for that kind of study.

A few notes, however, of a crystallographic character, kindly furnished by Mr. A. C. Spencer, of the Geological Department of this University, will give an idea of the nature of some of the substances in this respect.

As a rule, if the first crop of crystals was found to be uniform in appearance, they was subjected to chemical analysis, the determination of the halogen and the antimony being considered sufficient for the identification of the substance.

The results of the analyses of the compound formed from each mixture are placed in a table at the end of the description of these compounds.

Under each mixture is placed the results of the analysis of the compound obtained from that mixture, and in the smaller table is found the summary of the results of the analyses grouped under the formula of those compounds which the analyses seem to indicate have been formed.

The estimation of antimony was effected as follows: About 0.3 gram of the dried salt was weighed off, and after dissolving in a few cc. of a strong solution of tartaric acid, the whole was considerably diluted with water and heated to boiling. The solution was then acidified with sulphuric acid and a current of washed hydrogen sulphide passed into the solution for some time. When the antimony had been completely precipitated the liquid was heated for some time to drive off the hydrogen sulphide. The precipitate was then collected in a porcelain Gooch filter and washed successively with water, alcohol, ether, and carbon disulphide. The crucible was then dried in a hot-air bath, filled with carbon dioxide, gradually heated to 250°, and kept at that temperature for about an hour.

Experiments with Aniline Hydrochloride and Antimony Trichloride.

The account of the experiments with aniline hydrochloride and antimony trichloride will now be taken up in detail.

From mixture No. 1 (one part of the base to one of the metallic chloride), there crystallized out a colorless salt in thick irregular prisms, which on analysis gave results for chlorine and antimony, as recorded in Column 1 of Table I.

On comparing these results with the theoretical values which ought to be obtained if a compound called for by the one at the head of Column 1 had been formed, no agreement between these values was found, but as these experimental results did compare with the theoretical percentages of the compound heading Column 5, it was concluded that a compound was formed, having the composition expressed by the formula $(C_6H_5.NH_2.HCl)_3.SbCl_3.H_2O$, which may be called trianiline chlorantimonite.

Properties of the Compound.

This substance crystallizes in thick, colorless, monoclinic prisms, having the appearance shown in Fig. 1.

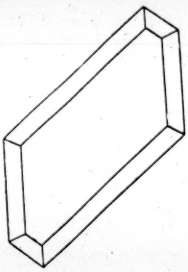


Fig. 1.

The action of a number of solvents was tried, and it was found to dissolve quite readily even in all the dilute mineral acids as well as in a number of organic acids in concentrated form; *e.g.*, tartaric and acetic acids. It required rather strong ethyl and methyl alcohol to effect solution.

Water or dilute alcohol precipitated a white antimonyl compound.

On boiling a solution of the salt the odor of nitrophenol was given off.

On gently heating the dry substance in an open tube it was rapidly decomposed, hydrochloric acid being given off.

After exposure to the air for several days the substance acquired an opaque greenish appearance. On keeping specimens for several months no further change in appearance seemed to occur.

The results of an analysis of mixture No. 2, in which the constituents were combined in the proportion of 1 molecule of aniline hydrochloride to 2 molecules of antimony trichloride, pointed to a compound of the formula

$$C_6H_5.NH_2.HCl.SbCl_3.H_2O.$$

Monaniline chlorantimonite crystallized out in long, thin, colorless plates. In general it was found to be similar to the first salt described.

Analyses of mixture No. 3 showed that monaniline chlorantimonite was again formed.

Mixtures 4, 5, and 7, each in turn, produced one and the same compound; *viz.*, trianiline chlorantimonite, the one first described above.

The results recorded include the analyses of both first and second crops, but in no case were the second crops found different from the first.

Table I.—Salts of Aniline Hydrochloride and Antimony Trichloride.

		I.		II.		III.		IV.		V.	
		$C_6H_5.NH_2.HCl.SbCl_3.$	$C_6H_5.NH_2.HCl.SbCl_3.H_2O.$	$C_6H_5.NH_2.HCl(SbCl_3)_2.$	$C_6H_5.NH_2.HCl(SbCl_3)_2.H_2O.$	$C_6H_5.NH_2.HCl(SbCl_3)_3.$	$C_6H_5.NH_2.HCl(SbCl_3)_3.H_2O.$	$(C_6H_5.NH_2.HCl)_3SbCl_3.$	$(C_6H_5.NH_2.HCl)_3SbCl_3.H_2O.$	$(C_6H_5.NH_2.HCl)_3SbCl_3.$	$(C_6H_5.NH_2.HCl)_3SbCl_3.H_2O.$
Theor.											
	Sb	33.70	32.08	41.20	39.96	44.49	4.53	24.70	23.83	19.51	18.95
	Cl	39.88	37.97	42.66	41.38	43.88	42.92	36.56	35.25	34.63	33.65
Exp.											
	Sb	19.18	...	....	....	32.71	....	19.01	....	....	19.05
	Cl	....	33.31	....	....	37.54	....	....	....	....	33.54
	Sb	19.93	19.74	34.11	34.65	32.62	32.66	19.50	19.28	....	19.18
	Cl	....	33.69	37.36	37.47	38.08	38.13	33.63	33.77	....	33.50
	Sb	....	....	33. 90	....	....	....	....	....	....	19.10
	Cl	....	....	37.46	....	....	....	....	....	....	33.24
	Sb	....	....	....	....	....	....	....	....	....	19.08
	Cl	....	....	....	....	....	....	....	....	....	33.29

Summary of Aniline Hydrochloride and Antimony Trichloride Salts.

	I. $[C_6H_5.NH_2.HCl.SbCl_3.H_2O.]$		V. $[(C_6H_5.NH_2.HCl)_3SbCl_3.H_2O.]$	
	Sb.	Cl.	Sb.	Cl.
Theor.	32.08	37.97	18.95	33.65
Exp.	32.71	38.08	19.05	33.54
	32.62	38.13	19.18	33.50
	32.66	37.54	19.10	33.24
	33.51	37.36	19.08	33.29
	33.90	37.47	19.01	33.63
	....	37.38	19.50	33.77
	....	37.46	19.28	33.31
	....	....	19.18	33.23
	....	....	19.74	33.69
	....	....	19.93	33.33
	....	....	18.88	....

Experiments with o-Toluidine Hydrochloride and Antimony Trichloride.

Experiments were next undertaken in the *o*-toluidine series, the line of work being carried out in a manner similar to that followed in the experiments with aniline.

The analyses of the compounds resulting from the several mixtures in this series point to the existence of only one compound, *viz.*, di-*o*-toluidine chlorantimonite, having the composition expressed by the formula $(C_6H_4.CH_3.NH_2.HCl)_2.SbCl_3$.

A large quantity of colorless crystals separated out from mixture No. 5, which, when dissolved and treated with hydrogen sulphide, gave no reaction for antimony.

The substance was the halide of the base. On pouring off the mother-liquor from these crystals, a compound of a different form at once separated out, which proved to be the double salt above mentioned. This substance, as usually formed, did not differ much in appearance from the aniline salts already described.

When allowed to form rapidly the tendency of both the aniline and all the toluidine chlorantimony salts is to crystallize out in beautiful sheaf-like masses with a satin luster.

The analytical results of the study of this series are placed in Table II:

Table II.—Salts of o-Toluidine Hydrochloride and Antimony Trichloride.

	I.		II.		III.		IV.		V.		VI.
	$C_6H_4.CH_3.NH_2.HCl.SbCl_3$.	$C_6H_4.CH_3.NH_2.HCl.SbCl_3.H_2O$.	$C_6H_4.CH_3.NH_2.HCl(SbCl_3)_2$.	$C_6H_4.CH_3.NH_2.HCl(SbCl_3)_2.H_2O$.	$C_6H_4.CH_3.NH_2.HCl(SbCl_3)_3$.	$C_6H_4.CH_3.NH_2.HCl(SbCl_3)_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HCl)_2SbCl_3$.	$(C_6H_4.CH_3.NH_2.HCl)_2SbCl_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HCl)_3SbCl_3$.	$(C_6H_4.CH_3.NH_2.HCl)_3.SbCl_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HCl)_6.SbCl_3$.
Theor.											
Sb	32.43	..	40.23	..	....	..	23.36	22.57	18.26	..	....
Cl	38.38	..	....	..	....	..	34.56	33.39	32.42	..	....
Exp.											
Sb	23.96	..	25.03	..	25.60	..	23.65	....	24.06	..	....
Cl	34.48	..	34.83	..	34.97	..	34.24	....	34.40	..	25.6
Sb	23.92	..	24.99	..	25.23	..	23.73	....	24.14	..	....
Cl	34.52	..	34.84	..	34.85	..	34.41	....	34.87	..	....

Summary of o-Toluidine and Antimony Trichloride Salts.

	IV. $(C_6H_4.CH_3NH_2.HCl)_2SbCl_3$.)	
	Sb.	Cl.
Theor.	23.36	34.56
Exp.	23.65	23.96	34.24	34.87
	23.73	23.92	34.41	34.83
	....	....	34.48	34.84
	....	....	34.52	34.97
	....	....	34.40	34.85

Experiments with m-Toluidine Hydrochloride and Antimony Trichloride.

As in the case of experiments with *o*-toluidine, the hydrochloride of the *m*-base was mixed in various proportions with the chloride of antimony. On an examination of the compounds obtained from each of the seven mixtures made, only

two substances were found which proved to be different from each other. Each of the seven mixtures, except the third, gave a compound having the formula

$$(C_6H_4.CH_3.NH_3HCl)_3.SbCl_3,$$

which should be named tri-*m*-toluidine chlorantimonite.

This substance always crystallized in thin orthorhombic tablets in the form of radiating groups, and perfectly transparent and colorless.

Following is a brief crystallographic account of one of the crystals examined :

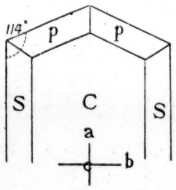


Fig. 2.

Orthorhombic.

C = basal plane.
p = brachypinacoids.
S = macrodomes.
C = ℭ.

Mixture No. 3 gave a compound which on analysis pointed to a substance whose composition should be expressed by the formula

$$(C_6H_4.CH_3.NH_2.HCl)_2.SbCl_3.H_2O,$$

di-*m*-toluidine chlorantimonite.

An analysis of one sample of the substance pointed to the previous substance without water of crystallization. The only form in which this compound was obtained was in fine granular crystals.

The results of experiments with *m*-toluidine compounds are recorded in Table III.

Table III.—Salts of m-Toluidine Hydrochloride and Antimony Trichloride.

	I.		II.		III.			IV.		V.		VI.	VII.
	$C_6H_4.CH_3.NH_2.HCl.SbCl_3.$		$C_6H_4.CH_3.NH_2.HCl.SbCl_3.H_2O.$		$C_6H_4.CH_3.NH_2.HCl(SbCl_3)_2.$		$C_6H_4.CH_3.NH_2HCl(SbCl_3)_2.H_2O.$	$C_6H_4.CH_3.NH_2.HCl)_2SbCl_3.$	$(C_6H_4.CH_3.NH_2.HCl)_2SbCl_3.H_2O.$	$(C_6H_4.CH_3.NH_2.HCl)_3.SbCl_3.$	$(C_6H_4.CH_3.NH_2.HCl)_3SbCl_3.H_2O.$	$(C_6H_4.CH_3.NH_2.HCl)_4SbCl_3.$	$(C_6H_4.CH_3.NH_2.HCl)_6SbCl_3.$
Theor.													
Sb	32.43	..	40.23	..	....	....	....	23.36	22.57	18.26	..	....	....
Cl	38.38	..	....	..	....	....	....	34.56	33.39	32.42	..	....	....
Exp.													
Sb	19.87	..	18.69	..	20.65	23.11	22.56	....	18.76	18.82	..	18.65	17.97
Cl	32.51	..	32.58	..	33.19	34.08	33.14	....	32.35	32.25	..	32.65	31.97
Sb	19.73	..	18.66	..	20.71	....	22.51	....	18.78	18.79	..	18.61	....
Cl	32.41	..	32.43	..	33.28	....	33.43	....	22.19	32.69	..	32.29	....

Summary of m-Toluidine Hydrochloride and Antimony Trichloride Salts.

	V. $[(C_6H_4.CH_3.NH_2.HCl)_3SbCl_3.]$				VI. $[(C_6H_4.CH_3.NH_2.HCl)_2SbCl_3.H_2O.]$	
	Sb.		Cl.		Sb.	Cl.
Theor.	18.61		32.42		22.57	33.39
Exp.	18.61	18.78	32.29	32.41	22.56	33.14
	18.65	18.69	32.35	32.58	22.51	33.43
	18.82	18.66	32.25	32.43	23.11	34.08
	18.79	17.97	32.69	32.51	....	33.19
	18.76	19.03	32.35	31.97	....	33.28
	....	....	32.19	32.31	....	....

Experiments with p-Toluidine Hydrochloride and Antimony Trichloride.

The compounds obtained in this group are di-*p*-toluidine chlorantimonite, $(C_7H_7.CH_3.NH_2.HCl)_2SbCl_3.\frac{1}{2}H_2O$, and tri-*p*-toluidine chlorantimonite, $(C_7H_7.CH_3.NH_2.HCl)_3SbCl_3.H_2O$.

Mixtures 1, 2, 3, and 4 produced the second of the above compounds, while the first was formed only by mixture 5. The tri-compound forms in colorless granular crystals, while the di-compound is formed in long, colorless, silky needles. Neither of these compounds seems to undergo any change on being kept for months.

The analytical results are recorded in the following table and summary:

Table IV.—Salts of p-Toluidine Hydrochloride and Antimony Trichloride.

	I.		II.		III.		IV.		V.	
	$C_6H_4CH_3.NH_2.HCl.SbCl_3$.	$C_6H_4CH_3.NH_2.HCl.SbCl_3.H_2O$.	$C_6H_4CH_3.NH_2.HCl(SbCl_3)_2$.	$C_6H_4CH_3.NH_2.HCl(SbCl_3)_2.H_2O$.	$C_6H_4CH_3.NH_2.HCl(SbCl_3)_3$.	$C_6H_4CH_3.NH_2.HCl(SbCl_3)_3.H_2O$.	$(C_6H_4CH_3.NH_2.HCl)_2.SbCl_3$.	$(C_6H_4CH_3.NH_2.HCl)_2.SbCl_3.H_2O$.	$(C_6H_4CH_3.NH_2.HCl)_3.SbCl_3$.	$(C_6H_4CH_3.NH_2.HCl)_3.SbCl_3.H_2O$.
Theor.										
Sb	32.43	..	40.23	..	....	..	23.36	22.97	18.26	17.77
Cl	38.38	..	....	..	....	..	34.56	33.95	32.42	31.55
Exp.										
Sb	23.68	..	23.40	..	23.68	..	....	22.09	18.27	....
Cl	33.52	..	33.66	..	33.16	..	....	33.13	31.54	....
Sb	23.58	..	23.50	..	24.03	..	....	22.61	18.21	....
Cl	33.49	..	33.38	..	33.08	..	....	33.10	28.14	....
Sb	....	..	....	..	....	..	....	....	18.27	....
Cl	33.10	..	....	..	....	..	....	....	31.46	....
Sb	....	..	....	..	....	..	....	....	18.11	....
Cl	....	..	....	..	....	..	....	....	31.55	....

Summary of p-Toluidine Hydrochloride and Antimony Trichloride Salts.

	IV. $(C_6H_4.CH_3.NH_2.HCl)_2.SbCl_3.\frac{1}{2}H_2O.$				V. $(C_6H_4.CH_3.NH_2.HCl)_3.SbCl.H_2O.$			
	Sb.		Cl.		Sb.		Cl.	
Theor.	22.97		33.95		17.77		31.55	
Exp.	23.68	23.50	33.52	33.66	18.27	18.27	31.54	31.55
	23.58	23.68	33.49	33.38	18.21	18.11	....	31.46
	23.40	24.03	....	....	....	....	....	....

Experiments with Aniline Hydrobromide and Antimony Tribromide.

The following series of mixtures of the above substances were made in hydrobromic acid solution: 1 : 1, 1 : 2, 1 : 3, 2 : 1, 3 : 1, 4 : 1, and 6 : 1.

In beaker No. 1 there was formed a copious crop of fine, light-yellow needles. In No. 2 there was a scant crop of two kinds of crystals, one kind being thin, flat, rectangular plates; the other yellow, granular crystals. Mixture 3 gave yellow needles, similar in appearance to those in No 1. In beaker 4 was formed a small crop of yellow needles along with larger yellow, granular crystals. A copious crop of light-yellow, scaly crystals was found in beaker 5. In No. 6 appeared a copious crop of yellow, granular crystals. A copious crop of irregular, flat, thick, whitish-yellow plates formed in beaker 7.

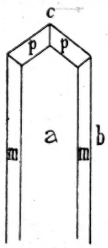


Fig. 3.

As in each case, the crystals had formed too quickly to be well defined and uniform, all the crops were redissolved, the solutions somewhat diluted, and again set aside to crystallize out.

The next series of crystals were generally of better form. Salts from beakers 1, 2, 3, 4, and 5 crystallized out in centimeter-long, canary-yellow, lath-shaped crystals of the orthorhombic system and of the form shown in the accompanying figure.

The cleavage is parallel to *a*. The crystals also showed parallel extinction in polarized light.

A chemical analysis of each of these five crops resulted in pointing to only one chemical compound, which is represented by the formula $(C_6H_5.NH_2.HBr)_3SbBr_3$, and receives the name dianiline bromantimonite.

It is of a canary-yellow color and translucent, stable in the air, undergoing no perceptible change on being kept for several months. The analyses showing its composition are given in the following table :

Mixtures 6 and 7 produced substances, which though of the same yellow color, differed markedly in their crystal habit. This will be best indicated by the figure. Cleavage is parallel to *a* and perfect. Habit tabular and perpendicular to *a*. Orthorhombic system.

a = brachypinacoid.
c = basal plane.
p = macropinacoids.
m = macroprisms.

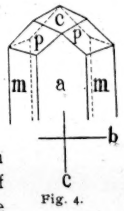


Fig. 4.

An analysis of this salt showed it to have an unusual composition, there being 4 molecules of the halide of the base combined with 1 molecule of the halide of antimony.

Its composition is expressed by the formula $(C_6H_5.NH_2.HBr)_4SbBr_3.H_2O$, and the compound receives the name tetraniline bromantimonite.

It was found impossible to determine the water of crystallization by exposure of the substance over sulphuric acid, as after a short treatment of this kind dense fumes of hydrobromic acid were given off.

On preserving crystals of the substance for some time they gradually became opaque.

The results of the above experiments are recorded in Table V :

Table V.—Salts of Aniline Hydrobromide and Antimony Tribromide.

	I.	II.	III.	IV.		V.	VI.		VII.
	$C_6H_5.NH_2.HBr.SbBr_3$.	$C_6H_5.NH_2.HBr.SbBr_3.H_2O$.	$C_6H_5.NH_2.HBr(SbBr_3)_2$.	$C_6H_5.NH_2.HBr(SbBr_3)_2.H_2O$.	$C_6H_5.NH_2.HBr(SbBr_3)_3$.	$C_6H_5.NH_2.HBr(SbBr_3)_3.H_2O$.	$(C_6H_5.NH_2.HBr)_3SbBr_3$.	$(C_6H_5.NH_2.HBr)_3SbBr_3.H_2O$.	$(C_6H_5.NH_2.HBr)_4SbBr_3$.	$(C_6H_5.NH_2.HBr)_4SbBr_3.H_2O$.	$(C_6H_5.NH_2.HBr)_6SbBr_3$.	$(C_6H_5.NH_2.HBr)_6SbBr_3.H_2O$.
Theor.												
Sb	22.47	26.85	28.71	16.95	16.53	13.60	11.36	11.17	8.55	
Br	59.93	62.64	63.79	56.49	55.10	54.42	53.03	52.14	51.28	
Exp.										
Sb	16.74	17.45	16.53	16.77	....	16.40	....	11.26	11.06	
Br	56.75	57.05	56.02	56.56	....	56.39	....	52.26	52.16	
Sb	....	11.59	16.34	....	....	....	....	...	11.24	
Br	....	54.80	58.82	....	....	....	....	....	51.97	
Sb	....	....	....	....	....	....	....	....	11.07	
Br	....	....	....	....	....	....	....	....	52.22	

Summary of Aniline Hydrobromide and Antimony Tribromide Salts.

	IV. $(C_6H_5.NH_2.HBr)_2SbBr_3$.		VI. $(C_6H_5.NH_2.HBr)_4SbBr_3.H_2O$.	
	Sb.	Br.	Sb.	Br.
Theor.	16.95	56.49	11.17	52.14
Exp.	16.74	56.75	11.06	52.16
	16.45	57.05	11.24	51.97
	16.53	56.02	11.07	52.12
	16.34	55.82	11.26	52.26
	16.77	56.56	....	....
	16.40	56.39	....	....

Experiments with o-Toluidine Hydrobromide and Antimony Tribromide.

From the seven mixtures which were made, judging by the appearance of the crystals formed, only one kind of compound seemed to be produced. The crystals of this substance had the same general appearance in each beaker, being of a light-yellow color. The crystallizing force of the substance seemed

to be weaker than that of any of the compounds previously analyzed.

Small, short, blunt prisms crystallized out, both as first and second crops, from the same mixture.

Determinations of antimony and bromine led to the conclusion that tri-*o*-toluidine bromantimonite $(C_6H_4.CH_3.NH_2.HBr)_3SbBr_3$, was the only compound formed from the constituents employed.

Table VI.—Salts of o-Toluidine Hydrobromide and Antimony Tribromide.

	I.		II.		III.		IV.		V.		VI.		VII.	
	$C_6H_4.CH_3.NH_2.HBr.SbBr_3$.	$C_6H_4.CH_3.NH_2.HBr.SbBr_3.H_2O$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_2$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_2.H_2O$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_3$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_2SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_2SbBr_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_3SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_3SbBr_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_4SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_4SbBr_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_6SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_6SbBr_3.H_2O$.
Theor.														
Sb	21.89	21.20	26.43	25.92	28.39	27.99	16.30	15.91	12.98	12.74	10.80	10.62	8.06	7.97
Br	58.39	....	61.56	....	63.09	....	54.35	53.05	51.95	50.95	50.36	49.56	....	...
Exp.														
Sb	....	....	13.37	....	12.80	....	12.67	....	12.87	....	12.78	....	12.86	...
Br	50.63	....	51.70	....	50.62	....	50.76	....	51.71	....	51.26	....	51.41	...
Sb	....	....	....	....	....	....	....	....	....	....	....	....	....	...
Br	50.57	....	....	....	51.84	....	51.57	....	....	....	....	....	51.51	...
Sb	13.17	....	....	....	....	....	....	....	....	....	....	....	....	...
Br	51.07	....	....	....	....	....	....	....	....	....	....	....	....	...

Summary of o-Toluidine Hydrobromide and Antimony Tribromide Salts.

	V. $(C_6H_4.CH_3.NH_2.HBr)_3SbBr_3$.			
	Sb.		Br.	
Theor.	12.98		51.95	
Exp.	13.17	12.87	51.70	51.70
	13.37	12.78	51.84	51.26
	12.80	12.86	51.07	51.51
	12.67	....	51.57	51.41

Experiments with m-Toluidine Hydrobromide and Antimony Tribromide.

Out of the seven combinations made only one compound was found. This substance crystallized out in each beaker in long, very pale-yellow, silky needles. The air-dried salt was more opaque and yellower than when seen in the mother-liquor. An analysis of the result of each mixture pointed to one compound only, and this has the composition expressed by the formula $(C_6H_4.CH_3.NH_2.HBr)_2SbBr_3$, and called di-*m*-toluidine bromantimonite.

Table VII.—Salts of m-Toluidine Hydrobromide and Antimony Tribromide.

	I.		II.		III.		IV.		V.		VI.		VII.	
	$C_6H_4.CH_3.NH_2.HBr.SbBr_3$.		$C_6H_4.CH_3.NH_2.HBr.SbBr_3.H_2O$.		$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_2$.		$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_2.H_2O$.		$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_3$.		$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_3.H_2O$.		$(C_6H_4.CH_3.NH_2.HBr)_2SbBr_3$.	
Theor.														
Sb	21.89	21.20	..	26.43	..	28.39	..	16.30	..	12.98	..	10.80	..	8.06
Br	58.39	56.53	..	61.56	..	63.09	..	54.35	..	51.95	..	50.36	..	...
Exp.														
Sb	15.89	....	..	....	..	15.65	..	16.66	..	....	..	16.45	..	15.96
Br	54.27	....	..	54.49	..	54.27	..	54.38	..	54.03	..	54.93	..	54.20
Sb	....	....	..	....	..	....	..	16.31	..	....	..	....	..	....
Br	....	....	..	54.86	..	....	..	54.49	..	53.93	..	....	..	54.25

Summary of m-Toluidine Hydrobromide and Antimony Tribromide Salts.

IV.

$(C_6H_4.CH_3.NH_2.HBr)_2SbBr_3$.

	Sb.		Br.	
Theor.	16.30		54.35	
Exp.	16.31	15.96	54.49	54.20
	16.66	15.89	54.86	54.25
	16.45	15.65	54.38	54.27
	....	....	54.03	54.27
	....	....	53.93	54.93
	....	....	54.49	....

Experiments with p-Toluidine Hydrobromide and Antimony Tribromide.

The mixtures of the constituents were made in the usual way in hydrobromic acid solution. Mixtures 1, 2, 4, 5, and 7 all gave crops of silver-white needles.

Repeated attempts were made to get a salt from mixture No. 6, but it was possible only to obtain the *p*-toluidine hydrobromide from the solution.

Mixture No. 3 gave a crop of very small lemon-yellow plates.

Owing to the ease with which the white salts give up or take up water of crystallization it was difficult to get sharp analytical data. The analyses of all the salts obtained seem to point to the existence of three different compounds, and one of them also with water of crystallization. They were as follows: Di-*p*-toluidine bromantimonite $(C_6H_4.CH_3.NH_2.HBr)_2.SbBr_3$; the same compound with 1 molecule of water of crystallization $(C_6H_4.CH_3.NH_2.HBr)_2.SbBr_4.HO$; tri-*p*-toluidine bromantimonite, $(C_6H_4.CH_3.NH_2.HBr)_3.SbBr_3$; and tetra-*p*-toluidine bromantimonite, $(C_6H_4.CH_3.NH_2.HBr)_4.SbBr_3$. In dry air these compounds are canary-yellow, but if exposed to the air on a damp day they change to snow-white. The compound which crystallized out from mixture 3, in the form of small plates, seems to be quite stable as to its color—it remains yellow constantly.

The yellow color can be restored in all three compounds by gently heating a portion on a piece of platinum foil.

The analyses of the compounds are tabulated in the usual manner in Table VIII.

Table VIII.—Salts of p-Toluidine Hydrobromide and Antimony Tribromide.

	I.		II.		III.		IV.		V.		VI.		VII.	
	$C_6H_4CH_3.NH_2.HBr.SbBr_3$.	$C_6H_4CH_3.NH_2.HBr.SbBr_3.H_2O$.	$(C_6H_4CH_3.NH_2.HBr)(SbBr_3)_2$.	$(C_6H_4CH_3.NH_2.HBr)(SbBr_3)_2.H_2O$.	$C_6H_4CH_3.NH_2.HBr(SbBr_3)_3$.	$C_6H_4CH_3.NH_2.HBr(SbBr_3)_3.H_2O$.	$(C_6H_4CH_3.NH_2.HBr)_2SbBr_3$.	$(C_6H_4CH_3.NH_2.HBr)_2SbBr_3.H_2O$.	$(C_6H_4CH_3.NH_2.HBr)_2SbBr_3$.	$(C_6H_4CH_3.NH_2.HBr)_2SbBr_3.H_2O$.	$(C_6H_4CH_3.NH_2.HBr)_4SbBr_3$.	$(C_6H_4CH_3.NH_2.HBr)_4SbBr_3.H_2O$.	$(C_6H_4CH_3.NH_2.HBr)_6SbBr_3$.	$(C_6H_5.CH_3.NH_2.HBr)_6SbBr_3.H_2O$.
Theor.														
Sb	21.89	21.20	26.43	25.92	28.39	27.99	16.30	15.91	12.98	12.74	10.80	10.62	8.06	7.97
Br	58.39	....	61.56	....	63.09	....	54.35	53.05	51.95	50.95	50.36	49.56	....	....
Exp.														
Sb	....	....	16.04	....	....	....	....	....	12.59	....	....	....	15.09	....
Br	....	....	52.73	....	54.78	....	....	. ..	51.45	....	....	....	52.90	....
Sb	....	....	15.73	....	....	....	10.85	....	....	....	....	....	....	....
Br	53.55	....	....	....	54.72	....	....	....	51.49	....	....	....	52.58	....
Sb	....	....	....	....	....	....	10.65	....	....	....	....	....	....	....
Br	53.94	....	....	....	54.54	...	49.83	....	....	....	....	....	....	....
Sb	....	....	....	....	....	....	....	....	....	....	....	....	....	....
Br	54.15	....	....	....	....	....	50.00	....	....	....	....	....	....	....
Sb	....	....	....	....	....	....	....	....	....	....	....	....	....	....
Br	53.70	....	....	....	....	....	....	....	....	....	....	....	....	....

Summary of p-Toluidine Hydrobromide and Antimony Tribromide Salts.

	IV.		V.		VI.	
	Sb.	Br.	Sb.	Br.	Sb.	Br.
Theor.	16.30	54.35	12.98	51.95	10.80	50.36
Exp.	....	53.94	12.59	51.45	10.85	50.00
	....	53.55	....	51.49	10.65	49.83
	....	54.15	....	....	....	....
	....	53.70	....	....	....	....
	....	54.78	....	....	....	....
	....	54.72	....	....	....	....
	....	54.54	....	....	....	....

On exposing the compound (which on analysis showed the presence of water of crystallization) in the desiccator over concentrated sulphuric acid, there was a constant loss of weight, due to the evolution of hydrobromic acid, presumably.

Experiments with Aniline Hydriodide and Antimony Triiodide.

Study in this series was begun with the aniline salt. Some difficulty was experienced here, since it was necessary to prepare hydriodic acid only in such quantities as would be immediately needed, owing to its rapid decomposition. It was also difficult to avoid the separation of free iodine when heating the mixtures.

The mixtures of the aniline and antimony halides were made up in the usual proportions hitherto employed.

A crop of finely divided, granular, scarlet crystals separated from mixture No. 1. On drying, these seemed to undergo no change. A determination of antimony and iodine clearly pointed to the existence of a compound whose composition is expressed by the formula $C_6H_5.NH_2.HI.SbI_3$, monaniline iodantimonite.

Out of mixture No. 2 small, almost microscopic, scarlet octahedra with modified edges crystallized out. An analysis of these revealed no new compound.

Crystals from mixture 3, again in the form of modified and twinned octahedra, proved on analysis to be identical with the first compound discovered in this series.

Mixtures 4 and 6 yielded nothing new in the way of double salts. Mixture No. 5, on the other hand, yielded a beautiful crop of fine carmine needles, which on analysis proved to be a combination not yet met with in the present investigation. The compound is composed of 3 molecules of aniline hydriodide and 2 molecules of antimony triiodide, expressed by the formula $(C_6H_5.NH_2HI)_3(SbI_3)_2$, trianiline diiodantimonite.

The last mixture examined was that in which the ratio of the constituents was 6 : 1. A new compound seemed to be formed here. The mixture from which the compound was finally obtained yielded at first only a large crop of the halide of the base. On evaporating the mother-liquor, a crop of

uniform golden-yellow plates was obtained. These were dried and tested for antimony. It was found to be present in considerable quantity. As soon as the crystals were drained off they began to undergo change in color from golden-yellow to orange-red. When dry they were analyzed and gave results pointing to the formula $(C_6H_5.NH_2.HI)_4SbI_3$, tetraniline iodantimonite.

The analytical results of the study of this series are given in Table IX.

Table IX.—Aniline Hydriodide and Antimony Triiodide.

	I.		II.	III.	IV.	V.	Va.	VI.	VII.
	$C_6H_5.NH_2.HI.SbI_3$.		$C_6H_5.NH_2.HI(SbI_3)_2$.	$C_6H_5.NH_2.HI(SbI_3)_3$.	$(C_6H_5.NH_2.HI)_2SbI_3$.	$(C_6H_5.NH_2.HI)_3SbI_3$.	$(C_6H_5.NH_2.HI)_3(SbI_3)_2$.	$(C_6H_5.NH_2.HI)_4SbI_3$.	$(C_6H_5.NH_2.HI)_6SbI_3$.
Theor.									
Sb	16.62	16.21	19.62	....	....	10.31	14.41	8.66	....
I	70.36	68.64	72.69	73.08	67.34	65.46	68.64	64.19	62.56
Exp.									
Sb	16.78	....	....	....	....	14.52	....	....	8.71
I	70.15	....	70.30	70.14	70.84	68.23	....	70.29	64.32
Sb	16.80	....	....	....	....	14.48	....	....	8.24
I	70.44	....	70.39	70.10	70.08	68.31	....	69.99	64.31
Sb	....	....	....	....	....	14.14	....	....	....
I	....	....	....	....	....	68.35	....	....	64.47
Sb	....	....	....	....	....	14.34	....	....	....
I	....	....	....	....	....	68.75	....	....	....

Summary of Aniline Hydriodide and Antimony Triiodide Salts.

	I.			Va.		VI.	
	Sb.	I.		Sb.	I.	Sb.	I.
Theor.	16.62	70.36		14.41	68.64	8.66	64.19
Exp.	16.78	70.15	70.10	14.52	68.23	8.71	64.32
	16.80	70.44	70.84	14.48	68.31	8.24	64.31
	....	70.31	70.08	14.14	68.35	...	64.47
	....	70.39	69.99	14.34	68.75	...	....
	....	70.14	70.29	....	....	...	....

Experiments with o-Toluidine Hydriodide and Antimony Triiodide.

The usual experiments were made with the above ingredients and no difficulty was experienced in obtaining well-characterized products in each experiment. The double salts which crystallized out from each of the first three mixtures had the same general appearance, consisting of short blunt needles of a brick-red color. Analyses of the three sets of crystals pointed to one and the same compound, containing 1 molecule of each of the original ingredients. The formula expressing the composition is shown by the following: $C_6H_4.CH_3NH_2.HI.SbI_3$, mon-*o*-toluidine iodantimonite.

An examination of the double salts formed from mixtures 4, 5, 6, and 7 indicated that a new variety had been formed. The appearance of the crystals in the above cases was quite different from that of the first compound described. They consisted of irregular-shaped, bronze-covered leaves. Analyses of a sample of each set indicated that only one individual had been formed, *viz.*, tri-*o*-toluidine diiodantimonite,

$$(C_6H_4.CH_3.NH_2.HI)_3.(SbI_3)_2.$$

Table X.—Salts of o-Toluidine Hydriodide and Antimony Triiodide.

	I.	II.		III.	IV.	V.	Va.	VI.	VII.
	$C_6H_4CH_3NH_2.HI.SbI_3$.	$C_6H_4CH_3NH_2.HI(SbI_3)_2$.	$C_6H_4CH_3NH_2.HI(SbI_3)_2.H_2O$.	$C_6H_4CH_3NH_2.HI(SbI_3)_3$.	$(C_6H_4CH_3NH_2.HI)_2SbI_3$.	$(C_6H_4CH_3NH_2.HI)_3SbI_3$.	$(C_6H_4CH_3NH_2.HI)_3(SbI_3)_2$.	$(C_6H_4CH_3NH_2.HI)_4SbI_3$.	$(C_6H_4CH_3NH_2HI)_6SbI_3$.
Theor.									
Sb	16.30	19.40	....	....	12.35	9.95	14.06	8.32	6.28
I	69.02	71.06	70.83	....	65.40	63.18	66.96	61.69	59.81
Exp.									
Sb	16.19	....	....	....	13.89	....	....	....	....
I	68.44	68.63	....	68.89	66.71	66.67	....	66.33	66.43
Sb	15.88	....	....	....	....	....	....	....	....
I	68.36	68.70	....	69.00	66.78	66.37	....	....	66.25

Summary of o-Toluidine Hydriodide and Antimony Triiodide Salts.

	I. $C_6H_4CH_3NH_2.HI.SbI_3$.			Va. $(C_6H_4CH_3NH_2.HI)_3(SbI_3)_2$.		
	Sb.	I.		Sb.	I.	
Theor.	16.30	69.02		14.06	66.99	
Exp.	16.19	68.44	68.70	13.89	66.71	66.25
	15.88	68.36	68.89	....	66.78	66.37
	....	68.63	69.00	....	66.33	66.67
	....	....	....	....	66.43	....

Experiments with m-Toluidine Hydriodide and Antimony Triiodide.

Mixtures of the above ingredients were made up in the usual way and well-defined crystals began to appear in each beaker as soon as the solutions were cool. On examination of the various sets of crystals, by means of the lens, they appeared to be all of the same general character. After removal from the solutions, and drying, the crystals were in the form of glistening, brick-red prisms.

Analysis pointed, in the case of each of the deposits, to the formation of only one chemical compound. This proved to be tri-*m*-toluidine diiodantimonite, having the formula

$$(C_6H_4.CH_3.NH_2.HI)_3.(SbI_3)_2.$$

This substance, like the corresponding ortho compound, seems to possess a strong crystallizing force. A statement of the analytical results leading to the above formula will be found in the following tables:

Table XI.—Salts of m-Toluidine Hydriodide and Antimony Triiodide.

	I. $C_6H_4CH_3.NH_2.HI.SbI_3$.	II. $C_6H_4.CH_3.NH_2.HI(SbI_3)_2$.	III. $C_6H_4CH_3.NH_2.HI(SbI_3)_3$.	IV. $(C_6H_4.CH_3.NH_2.HI)_2SbI_3$.	V. Va. $(C_6H_4.CH_3.NH_2.HI)_3SbI_3$. $(C_6H_4.CH_3.NH_2.HI)_3(SbI_3)_2$.	VI. $(C_6H_4.CH_3.NH_2.HI)_4SbI_3$.	VII. $(C_6H_4.CH_3.NH_2.HI)_6SbI_3$.
Theor.							
Sb	....	....	....	....	14.06	....	....
I	....	....	....	....	66.96	....	....
Exp.							
Sb	....	....	....	13.74	....	....	....
I	66.67	66.93	66.86	66.53	66.95	66.89	66.68
Sb	....	....	....	....	....	....	....
I	67.00	66.78	67.08	67.03	66.74	66.26	66.76

Summary of m-Toluidine Hydriodide and Antimony Triiodide Salts.

	Va. $(C_6H_4.CH_3.NH_2.HI)_3(SbI_3)_2$.		
	Sb.	I.	
Theor.	14.06	66.96	
Exp.	13.74	66.77	67.03
	....	67.00	66.95
	....	66.93	66.74
	....	66.78	66.89
	....	66.86	66.26
	....	67.08	66.68
	....	66.53	66.76

Experiments with p-Toluidine Hydriodide and Antimony Triiodide.

In working with this series some difficulty was met with in obtaining well-characterized and uniform crystals in the same beaker. From nearly every mixture worked with there crystallized out side by side light, orange-colored, blunt, pris-

matic crystals and darker, orange-colored needles. The prismatic forms seemed to be the more soluble of the two, and by regulating the concentration of the solution it was possible to obtain a uniform crop of the needle variety. Specimens of the light prismatic type were gotten out, but on being transformed to a porous earthenware plate, began to turn orange-red in a very short time.

Analyses of both kinds of crystals, after being dried in the air, showed that there was no difference in their composition. The composition of this compound, mono-*p*-toluidine iodantimonite, is expressed by the formula

$$C_7H_7.CH_3.NH_2.HI.SbI_3.$$

Table XII.—Salts of p-Toluidine Hydriodide and Antimony Triiodide.

	I.		II.		III.		IV.		V.		VI.		VII.	
	$C_6H_4.CH_3.NH_2.HI.SbI_3.$		$C_6H_4.CH_3.NH_2.HI.SbI_3.H_2O$		$(C_6H_4.CH_3.NH_2.HI)(SbI_3)_2.$		$(C_6H_4.CH_3.NH_2.HI)(SbI_3)_2.H_2O.$		$C_6H_4.CH_3.NH_2.HI(SbI_3)_3.$		$C_6H_4.CH_3.NH_2.HI(SbI_3)_3.H_2O.$		$(C_6H_4.CH_3.NH_2.HI)_2SbI_3.$	
Theor.														
Sb	16.30	....	....	....	19.40	....	19.12	....	....	..	12.35	..	9.95	..
I	69.02	67.37	....	....	71.06	....	70.83	....	....	..	65.40	..	63.18	..
Exp.														
Sb	....	....	....	....	16.58	....	....	....	16.88	..	16.08	..	....	..
I	69.12	....	....	....	68.86	....	....	....	....	..	....	..	68.51	..
Sb	....	....	....	....	16.27	....	....	....	....	..	16.75	..	....	..
I	69.30	....	....	....	68.67	....	....	....	....	..	....	..	68.43	..
Sb	....	....	....	....	....	....	....	....	....	..	16.34	..	....	..

	VI.		VII.	
	$(C_6H_4.CH_3.NH_2.HI)_4SbI_3.$		$(C_6H_4.CH_3.NH_2.HI)_4SbI_3.H_2O.$	
Theor.				
Sb	8.32	..	6.28	..
I	61.69	..	59.81	..
Exp.				
Sb	....	..	....	..
I	68.56	..	68.42	..
Sb	....	..	....	..
I	....	..	68.37	..
Sb	....	..	....	..

Summary of p-Toluidine Hydriodide and Antimony Triiodide Salts.

I.

$C_6H_4.CH_3.NH_3.HI.SbI_3$.

	Sb.		I.	
Theor.	16.30		69.02	
Exp.	16.58	16.08	69.12	68.43
	16.27	16.75	69.30	68.56
	16.88	16.34	68.86	68.42
	....	....	68.67	68.37
	....	....	68.51	....

ON THE RANCIDITY OF FATS.

By Iskar Nagel.

Under the direction of the late Prof. Benedikt, in Vienna, I carried on an investigation on the rancidity of fats and the refining of rancid oils and fats, and stated that these contain the following substances in variable quantities :

1. Free fatty acids, saturated as well as unsaturated.
2. Hydroxy acids of the fatty acid series.
3. Lactones and anhydrides of fatty acids.
4. Alcohols, as butyl, amyl, caproyl, and capryl alcohol.
5. Esters of saturated, of unsaturated, and of hydroxy acids of the fatty acid series with higher and sometimes also polybasic alcohols as butyl, caproyl, capryl alcohol, etc. ; glycol, etc.
6. Aldehydes, saturated, as butyric, caproic, caprylic aldehyde, etc., and unsaturated, as acrolein an oenanthic aldehyde.
7. Acetals, which are ether-like compounds of the above-mentioned aldehydes and alcohols.
8. Terpenes.

There may also be other substances present, but they could not be identified.

To remove these substances from a crude or rancid fat or oil, I proceeded as follows :

I. The free saturated and unsaturated acids, as well as the hydroxy acids, are easily removed by means of an aqueous solution of soluble glass. If the neutralization is effected with

sodium carbonate or with caustic soda, emulsions are obtained, and it is possible only by a long and tedious method to separate the oil from these emulsions, free from water and alkali. Emulsions are entirely avoided if, instead of the alkalies, an aqueous solution of glass is used. If such a solution is added to an oil or melted fat containing free acid, the acid unites with the bases of the silicates, and silicic acid is set free. The free silicic acid draws the alkali salts mechanically to the bottom, when it is impossible for them to be dissolved in the oil and to form an emulsion.

II. The lactones contained in the fats are more or less volatile with water vapor. Some of them, however, are insoluble in water and not volatile with water vapor. The volatile lactones are removed by the method described under VI. The non-volatile compounds must be converted into salts of hydroxy acids of the fatty acid series. This is accomplished by boiling for several hours the oil, which contains no free acid, with concentrated solutions of alkalies, as for instance, with a small quantity of a solution of sodium carbonate or of caustic soda. These then become visible in the oil, forming difficultly soluble flakes which fall to the bottom and are easily filtered off. These are the salts of the hydroxy acids.

III. The alcohols and esters of fatty acids and of hydroxy acids contained in fats and oils can be removed by the method described under VI, provided they are volatile with water vapor.

IV. Some of the aldehydes are volatile with water vapor and can be removed according to VI, while others are not, and these must be removed as follows: Four volumes of oil are heated for several hours with one volume of a concentrated solution of sodium bisulphite, and, after cooling, the aqueous solution is separated from the oil. It is known that the compounds of aldehydes with sodium bisulphite are usually solid, crystalline bodies, which are always slightly soluble in the solution of bisulphite. If the aldehydes are present only in small quantity no crystals are formed, and only a cloudy layer appears between the aqueous solution and the oil, or the solution, at first clear, becomes cloudy and contains the

compounds of the aldehydes with the sodium bisulphite in solution. These are removed together with the solution.

V. To remove the acetals, if they are not volatile with water vapor, I have found it best to heat the oil or fat for some time with dilute sulphuric acid. The higher acetals are decomposed by the sulphuric acid into alcohols and aldehydes, which are either volatile with water vapor and are removed according to VI or removed according to IV, if volatile. The acetals which are volatile with water vapor are removed according to VI.

VI. The terpenes are all volatile with water vapor and are removed by distillation with steam. It must be remembered that it is not always sufficient to conduct ordinary steam through the oil for the purpose of removing the volatile substances mentioned under 3–7, since it sometimes has a bad effect on the oil.

There are some substances which are not volatile or only very difficultly volatile with steam at 100° C., but which are more easily volatile with steam at a higher temperature. Hence, the distillation with steam at 100° C. would take a very long time, and even then would not entirely purify the oil. On the other hand, it is stated that the continuous contact of heated oils with steam or atmospheric air, while decomposing the fat, favors the formation of the substances named under 1–8.

These difficulties may be avoided in three ways:

a. By conducting steam together with some indifferent gas as hydrogen or carbon dioxide through the oil.

b. By conducting steam under diminished pressure through the oil.

c. By conducting steam heated gradually from 100°–170° C., together with an indifferent gas through the oil.

If this fractioning with superheated steam is made use of, those substances which are easily volatile are carried over first, before the more highly heated steam, which would decompose them, becomes necessary. It is well to let the oil cool *in vacuo* or in an atmosphere of some indifferent gas.

The method above described for purifying fats and oils is carried out in practice as follows: The fat or oil, freshly

pressed, extracted or already purified with sulphuric acid, is heated and thoroughly mixed with a concentrated solution of soluble glass, the quantity depending on the amount of free acid present, and is then filtered from the heavy precipitate which has settled to the bottom. The oil is now boiled with dilute sulphuric acid for about six hours. After cooling, the sulphuric acid is separated from the oil, which is washed again with a solution of soluble glass. The oil is then thoroughly mixed and heated with a fourth of its weight of a mixture of a concentrated solution of sodium carbonate and milk of lime (1 : 1) for several hours. In this process a very small quantity of the oil is saponified, and the soap thus formed sinks to the bottom. After cooling, the filtered oil is heated with a fourth of its weight of a concentrated solution of sodium bisulphite. The mixture is now allowed to cool, and the aqueous solution is separated from the oil, which is transferred to a distilling apparatus and subjected to distillation with steam, the temperature of which is gradually raised. Finally, the oil is allowed to cool in a current of carbon dioxide.

If the oil, before being subjected to the above method of purification, is carefully examined for those substances which are not glycerides of the fatty acids, or, if it is known that some of the substances above named (1–8) are not present, then such parts of the method as have for their object the removal of these substances, may be omitted. Further, the success of the method does not depend on the order of procedure described above. This may be changed at pleasure.

NOTE.

The Wax of the Bacillariaceae and Its Relation to Petroleum.

In a recent number of the *Berichte* (**32,** 2940) there is an article on this subject by Krämer and Spilker, an abstract of which is herewith given:

"The oil which has long been known to exist in the *Bacillariaceae* (Diatoms) had not been investigated until the authors undertook the task of tracing the probable relationship between it and mineral waxes and oils. These unicellular plants, whose siliceous coverings form immense deposits in

some places, are very abundant in peat-bogs. A quantity of the dried material was extracted with benzene, and yielded a brownish-black wax-like mass, which contained a high percentage of sulphur on account of the presence of the so-called 'sulphur bacteria', which set free this element from certain of its compounds. Fortunately, an immense deposit of material nearly free from sulphur was found at Ludwigshof. In the bed of a lake recently drained was a layer of diatom remains of an average thickness of 7 meters and covering an area of 900 hektares (2200 acres). This elastic, slimy mass contained about 10 per cent of dry substance. This yielded 3.6 per cent of wax when extracted, so that the amount obtainable from the entire deposit would be about 250,000 tons.

"The dark-brown wax was scarcely acted on by fuming nitric acid in the cold, but nearly 40 per cent dissolved on warming. The residue, when crystallized from alcohol, yielded a viscous oil, and a white solid in all respects similar to 'lekene', obtained from mineral wax by Beilstein and Wiegand.[1] When distilled the wax gave off methane, the oxides of carbon, sulphuretted hydrogen, and water, besides an oily distillate. Mineral wax (ozocerite) similarly heated gives off only traces of the oxides of carbon and sulphuretted hydrogen, and no water. It is very slightly saponified by alcoholic potash, but about 10 per cent of diatom wax is dissolved. From the alkaline solution ether extracts a brittle gum.

"When distilled under pressure, the two kinds of wax yield very similar products, except that the mineral wax yields no oxides of carbon, no water, and only traces of sulphuretted hydrogen, all of which are given off from diatom wax. In both cases unsaturated gaseous and liquid hydrocarbons are formed. When the liquid products are subjected to fractional distillation, the portions boiling between 130° and 290° are found to be identical.

"For comparison, Carnauba wax and Japan wax were distilled under the same conditions. The gaseous products resembled those from diatom wax, except for the absence of sulphuretted hydrogen, and the liquid distillates were practically identical with those above mentioned. In all four cases the middle fraction (130°–290°) had a molecular weight and composition agreeing fairly well with the formula $C_{11}H_{24}$. This was after the removal of the unsaturated constituents.

"The authors believe that mineral waxes and oils are formed from diatom wax by the combined action of heat, pressure, and ammonium carbonate (formed by the decay of

[1] Ber. d. chem. Ges., **16**, 1547.

protoplasm). Deposits such as that at Ludwigshof were probably formed in remote ages, and were covered by débris from the surrounding hills, so that great pressure would be exerted on the mass. The heat of the earth's interior would cause a distillation of the wax, and its transformation into the various kinds of petroleum, according to the conditions. The unsaturated hydrocarbons polymerized to form the viscous, heavy oils.

"It is hard to imagine conditions favorable to the accumulation of animal remains in sufficient abundance to form the petroleum deposits, but it is not difficult to believe that, in earlier ages, when the conditions for vegetation were so favorable, there might have been formed layers of diatomaceous material much larger than the one at Ludwigshof. It is not improbable, however, that certain petroleum deposits, *e. g.* in the oil shales, are of animal origin. Unfortunately, no remains of diatoms have been found in the oil sands or in the overlying rocks, but this may be due to the corroding action of ammonium carbonate on the very delicate siliceous coverings. Further, the overlying rock contains a very high percentage of silica, as it should if formed mainly of the remains of diatoms. O. N. Witt,[1] in discussing Engler's petroleum theory, suggested that diatoms ought possibly to be taken into account. Finally, however, he gave up the idea because no remains of diatoms have been found earlier than the tertiary deposits. The authors suggest that such remains would have been so corroded by percolating water in the course of ages that they would be unrecognizable.

"A. F. Stahl, also,[2] states that the theory of the formation of petroleum from animal fat is not supported by his observations in the Kalmuch and Kirgis steppes. He believes the oil was formed from diatoms, but made no experiments along this line.

"There may be points in regard to the above theory which geologists may object to, and it is evident that the correct solution of the problem cannot be attained without the aid of both geologists and chemists." C. E. W.

OBITUARY.

JOHANN CARL WILHELM FERDINAND TIEMANN.

News has recently reached us of the death of Prof. Tiemann, which occurred November 14. He was born in 1848 and took his Ph.D. degree at Göttingen in 1870. Since 1882 he has

[1] Prometheus, 1894, 349, 365.
[2] Chem. Ztg., Feb. 22, 1899.

been Professor of Chemistry in the University of Berlin and editor of the "*Berichte der deutschen chemischen Gesellschaft.*" He has always been active in the field of pure chemistry, his work on camphor being perhaps his best known contribution to the science. His energies have been, however, on account of his connection with the firm of Haarman & Reimer, especially directed toward the development of commercial products. He introduced artificial vanillin, prepared at first from coniferin and later from eugenol, and succeeded in perfecting a method for the preparation of ionone, a substance he had discovered and shown to be the essential principle of the odor of the violet. His work on the geraniol alcohols and citral is also a valuable contribution to that branch of the science. He was closely related by marriage to both Hofmann and Kuno Fischer. J. E. G.

REVIEWS.

THEORETISCHE CHEMIE. Vom Standpunkte der Avogadro'schen Regel und der Thermodynamik. Von DR. WALTER NERNST, o. Professor und Direktor des Instituts für physikalische Chemie an der Universität Göttingen. Zweite Auflage, mit 36 in den Text gedruckten Abbildungen. Stuttgart: Verlag von Ferdinand Enke. pp. 703. 1898.

The three great books which mark the progress of physical chemistry towards the close of the nineteenth century are the *Lehrbuch* and *Grundriss* of Ostwald, and the *Theoretische Chemie* of Nernst. The subject-matter is treated quite differently by Ostwald and by Nernst, and each of these works has its peculiar and distinctive advantage. The third edition of the *Grundriss* has just appeared, and the second edition of the *Lehrbuch*, though not completed, seems to be already exhausted. The second edition of the *Theoretische Chemie* has now appeared, just five years after the first. The method of treatment adopted by Nernst in the new edition is essentially the same as in the first. The volume is divided into four books: The General Properties of Substances; The Atom and Molecule; The Transformations of Matter; and The Transformations of Energy. But each book is enlarged, incorporating the work of the last few years. This applies especially to the sections on electrochemistry. This field, in which Nernst has played such a prominent rôle, was discussed very briefly in the first edition, presumably because of its exhaustive development by Ostwald in the Lehrbuch. In the new edition electrochemistry is treated more fully and in a broader way. A section is devoted to the general facts pertaining to electrolytic conduction, electrolysis, etc. This is

followed by an application of thermodynamics to the action of the cell, which we owe primarily to Helmholtz and Thomson. In this section paragraphs are devoted to the transformation of chemical energy into electrical, the calculation of electromotive force from thermodynamics, the application of thermodynamics to the lead accumulator. In the final section the application of the laws of osmotic pressure and the theory of electrolytic dissociation, to the problem of the electromotive force of elements, is made at some length. And this is the most interesting and important chapter in electrochemistry, since it has given us, for the first time, a rational theory of the cell. Paragraphs are devoted to the way in which currents are produced in solutions, solution of metals, theory of the origin of the galvanic current, concentration elements, the gas battery, etc.

The only criticism that can fairly be made is that the work is a masterpiece, containing new and original suggestions at every turn. But this is just what we should expect from a leader.

The lack of an adequate appreciation of the great merit of this work, manifested in a recent review in this country, is a source of deep regret to the writer of this notice.

HARRY C. JONES.